THE DIFFERENTIATION HISTORY OF THE EARTH BY RUBIDIUM-STRONTIUM ISOTOPIC RELATIONSHIPS

by

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ABSTRACT

The rubidium-strontium isotopic relationships in alkaline and subalkaline oceanic basalts have been determined by mass spectrometric techniques. The results are consistent with a complex model for the earth in which there is continuing convection.

Sr^{87}/Sr^{86} ratios for all oceanic basalts fall in a narrow range from .702 to .705. This suggests that the oceanic upper mantle source regions are generally uniform with respect to their Rb/Sr ratio and have been so for much of the earth's history. Inter-island variations in the Sr^{87}/Sr^{86} ratio indicate that minor heterogeneities in the Rb/Sr ratio were developed at the time of major differentiation of the mantle early in the Earth's history.

The subalkaline basalts dredged from the ocean floors and ridges have uniformly low strontium and rubidium concentrations and low Rb/Sr ratios. These ratios are too low to account for the observed Sr^{87}/Sr^{86} ratio and it is concluded that the subalkaline basalts are derivatives from material that had a significantly higher Rb/Sr ratio at an earlier stage of the Earth's development. To account for the present low Rb/Sr ratio, the suggestion is made that the source material, following the development of much of the radiogenic Sr^{87} now observed in these basalts, passed through a residual stage prior to the generation of the subalkaline magmas.

The shield-building tholeiites of the Hawaiian Islands have two- to three-fold enrichments in rubidium and strontium over their submarine counterparts although the Rb/Sr ratios are identical. In addition the shield-building tholeiites have considerably higher Sr^{87}/Sr^{86} ratios.

The alkaline basalts from the volcanic islands and the dredge basalts have very similar Sr^{87}/Sr^{86} ratios. This may indicate similar source materials for both magma types. The observed enrichment of rubidium and strontium and high Rb/Sr ratios relative to the subalkaline basalts is the result of the geologic processes, that combined to produce the magmas in recent time.

Hawaiian Island basalts are subdivided on the basis of their Sr^{87}/Sr^{86} ratios into the tholeiites, the alkali series (including a trachyte) and the nepheline basalts. The results are consistent with the derivations of these basalts from different depths from an upper mantle in which the Rb/Sr ratio decreases with increasing depth.

Thesis Supervisor: Patrick M. Hurley
Title: Professor of Geology

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PART I

RUBIDIUM-STRONTIUM ISOTOPIC RELATIONSHIPS IN OCEANIC BASALTS

ABSTRACT

Mass spectrometric analyses of strontium in oceanic basalts reveal that they are characterized by Sr^{87}/Sr^{86} ratios from .702 to .705. This is an indication of the Rb/Sr homogeneity of the upper mantle basalt source regions for much of the earth's history. Minor variations that are apparent in the Sr^{87}/Sr^{86} ratios of basalts from widely separated localities reflect minor Rb/Sr heterogeneities.

Subalkaline basalts from the oceanic ridges are characterized by low rubidium and strontium concentrations and low Rb/Sr ratios. In view of the observed Sr^{87}/Sr^{86} ratios it is concluded that these basalts are derivatives of a source region having a significantly higher Rb/Sr ratio. This implies that prior to the generation of the subalkaline magmas, the source material was depleted in rubidium relative to strontium. A residual stage in the development of the basalts could account for these relationships.

Tholeiitic basalts from the Hawaiian Islands have two- to three-fold enrichments of rubidium and strontium over their submarine counterparts although the Rb/Sr ratios are identical. The Sr^{87}/Sr^{86} ratios for the Hawaiian tholeiites are higher than these ratios for the submarine basalts. This may be a reflection of either lateral or vertical variations in the Rb/Sr

ratio in the upper mantle.

Alkaline basalts from the volcanic islands have similar Sr^{87}/Sr^{86} ratios to the subalkaline basalts. This may indicate similar source materials for both magma types. The observed enrichments of rubidium and strontium and high Rb/Sr ratios relative to the subalkaline basalts are the result of the geologic processes that combined to produce the magmas in Recent time.

The rubidium-strontium isotopic relationships in oceanic basalts are consistent with an asymmetrically differentiating earth with continuing convection.

INTRODUCTION

Introductory Statement

Various lines of evidence point to the upper mantle as being the source region for the oceanic basalts. These basalts are generally believed to be derived from the products of partial melting of an ultramafic upper mantle. Residual material remaining at depth may be similar to the alpine-type ultramafics. Recent analyses (Roe, 1964; Steuber and Murthy, 1966) have shown that these ultramafics, in particular the dunites, contain extremely low abundances of rubidium and strontium. From these results and from geochemical reasoning, it is concluded (Roe, 1964) that virtually all of the rubidium and strontium are partitioned into the fluid phases of geologic processes. Therefore the rubidium and strontium isotopic relationships of the derivative basalts should reflect the rubidium-strontium characteristics of their upper mantle source regions. This applies only to oceanic basalts because continental basalts appear to have been contaminated by crustal strontium and rubidium.

Alkaline basalts from the oceanic islands are also ruled out as candidates for studies of the upper mantle since they have undergone processes of differentiation during their formation. The key to this problem may be the extensive subalkaline oceanic basalts that occur on the mid-oceanic ridges, along the large

fracture zones in the ocean floors, and in the ocean basins. They appear to represent the predominant basalt magma produced in the upper mantle and from chemical criteria, appear to be the most primitive of all basalts. Until very recently, no rubidium-strontium analyses were reported for these basalts and what has become available in the past two years is scanty.

This investigation was undertaken to obtain more representative rubidium-strontium data for the subalkaline oceanic basalts from the shield-building volcanoes and from the ocean bottoms. In addition, further analyses of alkalic oceanic basalts were made. It has been attempted to relate the results obtained to possible major events in the Earth's evolutionary history.

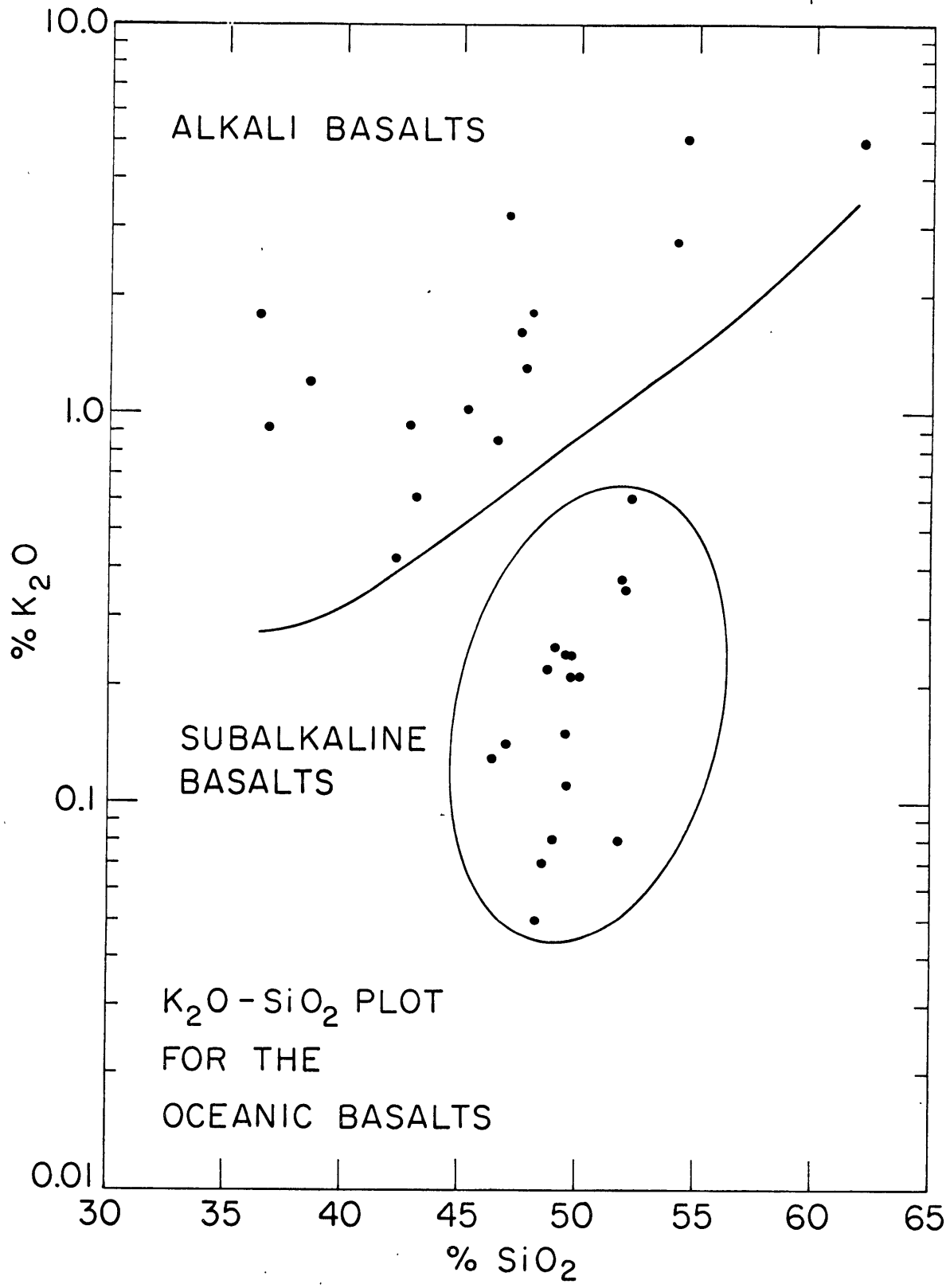
Subalkaline basalts dredged from the mid-Atlantic Ridge, East Pacific Rise, and Molokai Fracture zone as well as "tholeiites" from the Hawaiian Islands were selected for analysis of their rubidium and strontium concentrations and Sr^{87}/Sr^{86} ratios.

Further analyses were made on alkali basalts from Tristan da Cunha, the Canary Islands and Madeira, and the Hawaiian Islands. The Hawaiian Island specimens included nepheline-melilite basalts and a trachyte.

Many of the basalt samples had been previously analyzed for major oxides and potassium concentrations were determined from these analyses. The SiO_2-K_2O relationships for the analyzed samples, showing the separation of alkaline and tholeiite basalts are given in Figure 1.

FIGURE 1

K_2O-SiO_2 Relationships for the Oceanic Basalts


10.0
1.0
0.1
0.01
% K_2O
ALKALI BASALTS
SUBALKALINE
BASALTS
$K_2O - SiO_2$ PLOT
FOR THE
OCEANIC BASALTS
30
35
40
45
50
55
60
65
% SiO_2

Previous Work

Subalkaline Dredge Basalts. The great surge in oceanographic research that has occurred in the past decade has lead to extensive studies of the physical features of the oceanic ridges and the history and development of the ridges and basins (Menard, 1958, 1964; Hess, 1959, 1962, 1965; Heezen, Tharp and Ewing, 1959; Bott, 1965; Heirtzler and Le Pichon, 1965; van Andel, et al, 1965; and Ewing, Le Pichon, and Ewing, 1966).

Descriptions and analyses of basalts from the oceanic ridges are reported by Murray and Renard (1891), Correns (1930), Wiseman (1937), and Shand (1949), and more recently by Engel and Engel (1961, 1964a,b), Quon and Ehlers (1963), Moore and Reed (1963), Muir and Tilley (1964), Nicholls, Nalwalk and Hays (1964), Engel, Engel, and Havens (1965), Engel, Fisher and Engel (1965), Matthews, Vine and Cann (1965), Moore (1965), Nicholls (1965), and Melson, et al (1966). Rare earth distribution patterns are reported by Frey and Haskin (1964) and K/Rb ratios by Gast (1965).

Very few rubidium-strontium analyses of the sub-alkaline oceanic basalts are reported in the literature. Previous to this study, only six analyses were reported (Faure and Hurley, 1963 and Tatsumoto, Hedge, and Engel, 1965). The results of these studies are given in Table 1.

Table 1

Published Results of Rubidium-Strontium Studies of Subalkaline Oceanic Dredge Basalts

	Locality	$Sr^{87}/Sr^{86}]^N$	Rb ppm*	Sr ppm*	Rb/Sr
Atlantic	20°40'S 13°16'W	.7024[1]	1.14	134	0.0085
	5°47'S 11°25'W	.7027[1]	2.63	109	0.024
	9°39'N 40°27'W	.7021[1]	0.66	150	0.0044
	31°18'N 40°54'W	.7032[2]	9.25	118.3	0.0824
Pacific	12°52'S 110°57'W	.7016[1]	1.06	86	0.012
	18°25'S 113°20'W	.7017[1]	0.45	98	0.0045

*Determined by isotope dilution techniques

[1]Data from Tasumoto, Hedge, and Engel (1965). No standard data are given for comparison

[2]Data from Faure and Hurley (1963) relative to Sr^{87}/Sr^{86} = .7080 for standard $SrCO_3$.

Volcanic Islands. The alkali-rich and subalkaline basalts of the oceanic islands have been more extensively investigated than their submarine counterparts. In particular, the Hawaiian Islands are probably the most carefully studied sequence of oceanic basalts anywhere. Detailed petrologic, petrographic, and petrogenic relationships of these volcanics (Washington, 1923; Powers, 1935, 1955; Daly, 1944; Stearns, 1946; MacDonald and Powers, 1946; Winchell, 1947; Wentworth and Winchell, 1947; MacDonald, 1949; Tilley and Scoon, 1961; MacDonald and Katsura, 1964) reveal that the subalkaline basalts (tholeiites) and their derivatives form the broad base upon which these shield volcanoes are built and are capped by much smaller amounts of alkaline basalts.

Minor element studies of the Hawaiian Islands volcanic suites are reported by Wager and Mitchell (1953) and K/Rb ratios by Lessing, Decker and Reynolds (1963). Strontium isotope analyses reported for the Hawaiian basalts are quite numerous (Hedge and Walthall, 1963; Faure and Hurley, 1963; Lessing and Catanzaro, 1964; Powell, Faure, and Hurley, 1965; Hamilton, 1965a). Strontium analyses for other alkali basalts from the volcanic islands are reported by Faure and Hurley (1963), Gast, Tilton and Hedge (1964), Hamilton (1965b), McDougall and Compston (1965), Moorbath and Walker (1965), and Pushkar (1966).

Rubidium-Strontium System

General. For any system that has remained closed with respect to rubidium and strontium transfer across its boundaries, the relationship of the isotope composition of strontium with time following closure of the system is expressed by the standard equation:

$$Sr^{87}/Sr^{86}\Big]_t = Sr^{87}/Sr^{86}\Big]_o + Rb^{87}/Sr^{86}\Big]_t (e^{\lambda t} - 1) \qquad (1)$$

Where: t = age of the system in years

λ = the decay constant for Rb^{87} in reciprocal years

$Sr^{87}/Sr^{86}\Big]_t$ = atomic ratio of Sr^{87} to Sr^{86} at t years following the last closure of the system (t = present time).

$Sr^{87}/Sr^{86}\Big]_o$ = atomic ratio of Sr^{87}/Sr^{86} at instant system became closed (t = 0).

$Rb^{87}/Sr^{86}\Big]_t$ = atomic ratio of Rb^{87} to Sr^{86} at t years following last closure of the system (t = present time).

Equation (1) cannot be solved as it stands since there are two unknowns, t and $Sr^{87}/Sr^{86}\Big]_o$. If, however, the system is composed of at least two subsystems, an equation similar to (1) can be written for each subsystem. These equations

may be solved simultaneously for t since the $Sr^{87}/Sr^{86}\Big]_o$ ratio is identical for each subsystem.

Regression Lines. Because the abundance of Sr^{87}, generally expressed in terms of Sr^{87}/Sr^{86} ratios, increases at a rate dependent upon the abundance of Rb^{87} associated with it, it is possible to determine the characteristic of the development of Sr^{87}/Sr^{86} in the last evolutionary stage of any rock from its observed Rb/Sr and Sr^{87}/Sr^{86} ratios. This "evolution" of Sr^{87}/Sr^{86} for any given Rb/Sr ratio is expressed graphically as a function of time by a regression plot (Figure 2). The ratio $Sr^{87}/Sr^{86}\Big]_o$ is plotted as the ordinate and time from zero to 4.5 b.y. as the abscissa. The slope of the regression line is proportional to the Rb^{87}/Sr^{86} ratio. A practical example of regression diagrams is the determination of the time at which a series of comagmatic differentiates were formed from a parent magma. The Rb^{87}/Sr^{86} and Sr^{87}/Sr^{86} ratios for each differentiate are measured and plotted on the regression line diagram. Their point of intersection gives the age and strontium isotopic composition of the parent magma at the time of differentiation (Figure 2).

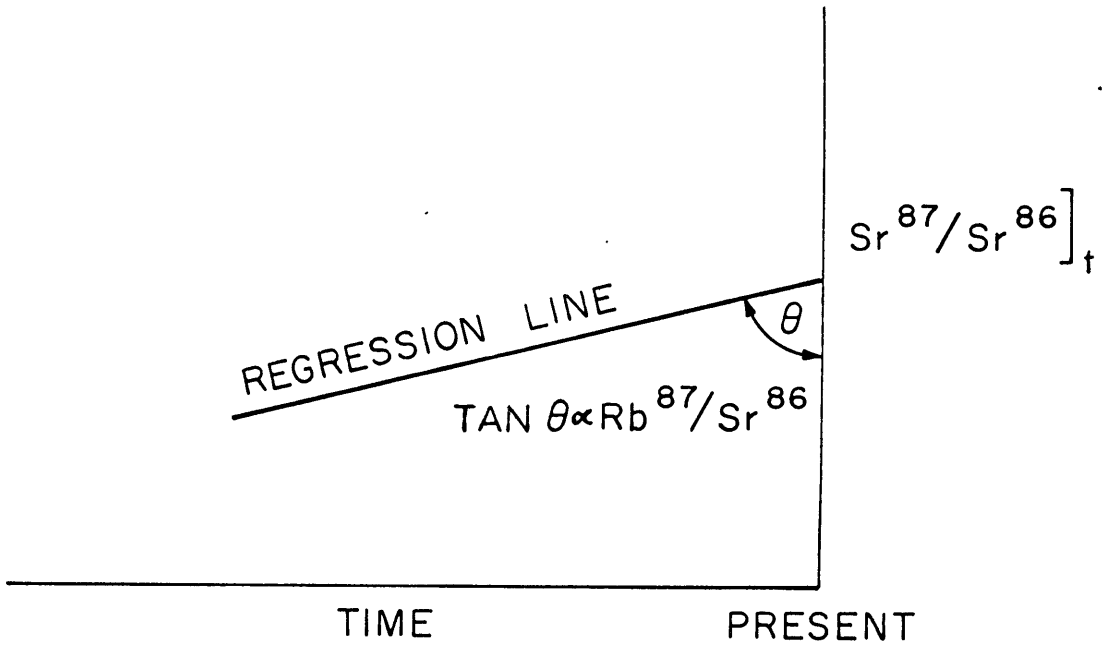
Regression line studies of recent basalts illustrate the last stage in Sr^{87}/Sr^{86} development of the magmas and, most important, their source regions in the upper mantle.

FIGURE 2

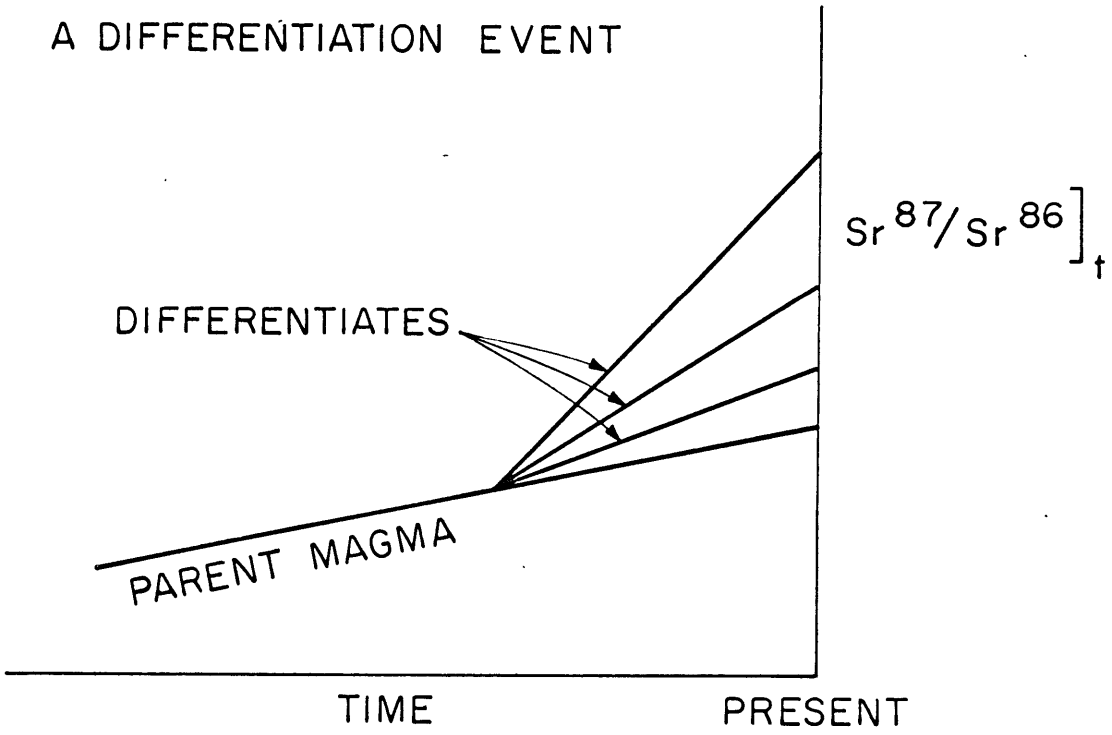
A. Sr^{87} Regression Diagram

B. A Differentiation Event

A. Sr^{87} REGRESSION DIAGRAM



B. A DIFFERENTIATION EVENT



Initial Ratios

The initial ratio of Sr^{87}/Sr^{86} for any chemical system is the ratio that system had at the instant it became closed to the transfer of rubidium and strontium across its boundaries. In the case where the chemical system is composed of a number of subsystems, for example the mineral phases in an igneous rock, the initial ratio for each subsystem as well as the major system is the same and may be determined from the simultaneous solution of equations similar to (1) written for each subsystem.

When there is only a single system present, the initial Sr^{87}/Sr^{86} ratio is found by correcting the observed ratio for the radiogenic strontium produced by Rb^{87} decay following closure of the system. This can be done only if the age of the system and the abundance of Rb^{87} is known. Recent basalts require no correction since there has not been a sufficient time lapse following closure of the system to produce a measurable increase in the radiogenic strontium. Therefore, the observed ratio in these basalts is the initial ratio.

ANALYTICAL TECHNIQUES

Chemistry and Mass Spectrometry

Rubidium and strontium concentrations were measured by isotope dilution techniques of mass spectrometry. The isotopic composition of strontium was determined both by isotope dilution measurements on spiked samples and by direct measurement on unspiked samples.

The procedure followed in preparing basalt samples for rubidium and strontium isotopic analysis are the standard methods adopted by the M.I.T. Geochronology Laboratory for samples with very low concentrations of rubidium and strontium and are described in the Annual Progress Reports (Shields, 1964; Roe, 1964; and by Pinson, et al, 1965). Spike solutions are added as the first step in the digestion process.

Both spiked and unspiked samples are dissolved in platinum dishes using 15 mls HF and 2 mls $HClO_4$ per gram of sample and taken to dryness. The solid residue is taken up in 100 mls of 2NHCl, evaporated to dryness, taken up in another 50 mls 2NHCl, evaporated to 10-15 mls, and diluted to 40-50 mls with demineralized water. Solid residues remaining at this stage are removed by filtering.

Separation of rubidium and strontium is accomplished on vycor ion exchange columns using Dowex 50-8x, 200-400 mesh, cation exchange resin, supported on a quartz-fiber mat.

Strontium collection is monitored by a carrier-free Sr^{85} tracer and rubidium by atomic absorption analyses.

Blanks are run periodically along with the samples to keep a close check on those contamination levels and to apply corrections to the rubidium and strontium measurements. Table 2 lists the results of blank analyses carried out through the period of this investigation.

Table 2

Contamination Levels for Rubidium and Strontium

Rb μgm/gm	Sr μgm/gm	Comments
.095	.024	Special distilled HF
.065	.015	"
.025		"
.008		"
Avg. .048 ± .020 μgm/gm	.020 ± .005 μgm/gm	
.046	.034	Commercial HF

The strontium and the majority of the rubidium isotope dilution measurements were made on a 60° sector, six-inch radius, single filament, solid source, single collector Nier-type instrument (Sally*). The ion beam is amplified by a

*For purposes of identification, each of the five mass spectrometers in the M.I.T. Geochronology Laboratory is assigned a name.

Carey Model 31 vibrating reed electrometer and the output is recorded on a Brown strip-chart recorder. The mass range is scanned mechanically by a reversing magnet sweep.

Subalkaline oceanic basalt rubidiums were analyzed on a Nuclide Corporation six-inch mass spectrometer (Nancy), modified to permit peak-hopping.

Strontium isotope ratios of the Canary Island suite and four dredge samples from the Molokai Fracture Zone were measured by P. M. Hurley on a 12-inch, 60° sector, triple filament instrument (Connie). This machine was built by the Consolidated Electrodynamics Corporation and is equipped with an expanded scale recorder which gives a higher degree of precision than that obtained for the six-inch machines.

Analytical Precision

Over a period of months, mass spectrometer characteristics may change significantly. For this reason, a standard strontium carbonate was run periodically (in practice, once every two weeks). The results are reported in Tables 3 and 4. In addition, replicate analyses on separate weighings of selected individual samples were conducted as further evidence for the authenticity of the measurements. The results of these analyses are reported in Tables 5 and 6.

Table 3

Analyses of Eimer and Amend Strontium Carbonate Standard on Sally Throughout the Period of This Investigation

Record No.	Date	No. Scans	86/88	87/86*	Analyst
4187(S)	4/14/65	72	.1189	.7079	RVS
4227(S)	7/20/65		.1186	.7084	MH
4262(S)	11/2/65	60	.1184	.7081	AEB
4264(S)	11/3/65	60	.1181	.7083	AEB
4265(S)	11/4/65	42	.1182	.7082	AEB
4367(S)	1/18/66	42	.1174	.7080	HWF
4520(S)	3/28/66	60	.1187	.7076	AEB
4557(S)	4/9/66	42	.1180	.7080	AEB
4624(S)	5/2/66	60	.1187	.7075	AEB
4662(S)	5/15/66	48	.1191	.7084	AEB
4669(S)	5/17/66	48	.1191	.7085	AEB
4728(S)	6/10,11/66	18	.1193	.7082	AEB,DGB
4762(S)	6/23,24/66	36	.1184	.7082	DGB

Average 86/88 $.1185 \pm .0005$ $2\sigma = .001$
87/86* $.7081 \pm .0003$ $2\sigma = .0006$

(S) mass spectrometer "Sally"

* normalized to $Sr^{86}/Sr^{88} = .1194$

RVS R. Van Schmus

MH M. Heath

HWF H. W. Fairbairn

AEB A. E. Bence

DGB D. G. Brookins

Table 4

Analyses of Eimer and Amend Strontium Carbonate Standard on Connie Throughout the Period of This Investigation

86/88	87/86*	Analyst
.1192	.7071	P. M. Hurley
.1192	.7076	"
.1193	.7079	"
.1192	.7081	"
.1190	.7077	"
.1190	.7076	"
.1192 $\pm$ .0001	.7077 $\pm$ .0003	
$2\sigma = \pm$ .0003	$2\sigma = \pm$ .0006	

*Normalized to $Sr^{86}/Sr^{88} = .1194$

Table 5

Reproducibility of Strontium Analyses

Sample No.	Sr^{87}/Sr^{86} | N Calculated	Diff x_1-x_2	Diff^2 $(x_1-x_2)^2$	Sr Conc.	Diff	Diff^2
JP 16	.7029 .7024	.0005	.00000025	1759 1746	13	169
9960	.7043 .7043	.0000	.00000000	2155 2145	10	100
R5950	.7018 .7039	.0021	.00000441	113.4 114.3	.9	.81
R5974	.7033 .7048	.0015	.00000225	135.97 135.70	.27	.073
			.00000791			269.883

$$S.D. = \sqrt{\frac{.00000791}{8}} = \pm .0010 \qquad S.D. = \sqrt{\frac{269.883}{8}} = \pm 6.7$$

Table 6

Reproducibility of Rubidium Analyses

Sample No.	Rb μgm/gm	Diff x_1-x_2	Diff^2 $x_1-x_2^2$
JP 16	46.5 46.7		
	46.6	.2	.0400
R5964	2.50 2.46		
	2.48	.04	.0016
R5965	2.61 2.61		
	2.61	.00	.0000
R5966	2.65 2.62 2.67		
	2.65	.05	.0025
R5967	2.87 2.90		
	2.89	.03	.0009
10396	0.50 0.50 0.46		
	0.49	.04	.0016

$$\text{S.D.} = \pm \sqrt{\frac{.0466}{12}} = \pm 0.062$$

Comparison of Calculated Sr^{87}/Sr^{86} with Measured Sr^{87}/Sr^{86} Ratios

Calculated Sr^{87}/Sr^{86} ratios are determined from the isotope dilution analyses by the method reported by Van Schmus (1966). Measured Sr^{87}/Sr^{86} ratios are obtained directly from the analyses of unspiked samples and are believed to closely approximate the true isotopic ratio. Selected suites of samples are analyzed both by isotope dilution and isotope ratio techniques to compare the two methods. These data are reported in Table 7. The measured Sr^{87}/Sr^{86} ratios were analyzed on a 12-inch machine (Connie) which gave a standard carbonate Sr^{87}/Sr^{86} ratio of .7077. The data are corrected to a Sr^{87}/Sr^{86} ratio of .7081 to bring them in line with the data from the 6-inch machine (Sally).

There does not appear to be any consistent significant differences between the calculated and measured isotope ratios.

Table 7

Comparisons of Calculated and Measured Sr^{87}/Sr^{86} Ratios

Sample No.	Sr^{87}/Sr^{86} N calculated (x_1)	Sr^{87}/Sr^{86} N^1 measured	Sr^{87}/Sr^{86} N^2 measured (x_2)	x_1-x_2	$x_1-x_2^2$
R5810	.7033	.7024	.7036(S)		
			.7028		
		Avg.	.7032	+.0001	.00000001
R5811	.7035	.7032	.7036	-.0001	.00000001
R5814	.7033	.7030	.7034	-.0001	.00000001
R5816	.7039	.7033	.7037	+.0002	.00000004
R5817	.7034	.7035	.7039	-.0005	.00000025
R5832	.7030	.7031	.7035	-.0005	.00000025
R5964	.7034	.7030	.7034	.0000	.00000000
R5966	.7039	.7028	.7031(S)		
			.7032		
		Avg.	.7032	+.0007	.00000049
					Σ .00000106

$$\sigma = \pm \sqrt{\frac{.00000106}{16}} = .0002^6 = \pm .0003$$

N Normalized to $Sr^{86}/Sr^{88} = .1194$

[1]Data from Connie; E and A standard carbonate $Sr^{87}/Sr^{86} = .7077$

[2]Connie data corrected to standard $Sr^{87}/Sr^{86} = .7081$

(S)Isotope Ratio analyzed on Sally.

RESULTS

Mid-Atlantic Ridge Dredge Basalts

The results of rubidium and strontium analyses for eleven mid-Atlantic Ridge dredge basalts having tholeiitic affinities are given in Tables 8 and 9. With only a few exceptions the Sr^{87}/Sr^{86} ratios are in the range .7028 to .7042 with the average .7037. The average Rb/Sr ratio is .0073 and from Figure 3 it is seen that the Sr^{87} regression lines projected back to 4.5 billion years fall considerably above the assumed primordial Sr^{87}/Sr^{86} ratio for the earth.

The average abundances of rubidium and strontium (0.98 ppm and 138.7 ppm respectively) are low compared to the majority of basaltic rocks. The combination of low rubidium and strontium concentrations, low Rb/Sr ratios, and the observed Sr^{87}/Sr^{86} ratios suggest that the upper mantle source region for these basalts was depleted in trace elements prior to the generation of the subalkaline magmas.

The potassium concentrations are calculated from the chemical analyses of these dredge basalts (Bence, 1966, Appendix A) and K/Rb ratios are determined (Table 9). These ratios are the highest observed for terrestrial material but fall over a wide range.

Table 8

Strontium Isotopic Composition of

Mid-Atlantic Ridge Dredge Basalts

Sample No.	Location	$Sr^{87}/Sr^{86}\Big\|_{C}^{N}$	Rock Type
R5953	5°47'S 11°25'W	.7033	
R5954	9°39'N 40°27'W	.7037	
R5955	9°39'N 40°27'W	.7042	
R5973	about 22°N	.7042	Greenstone
R5974	about 22°N	.7041(2)	Fresh basalt
R5975	about 22°N	.7028	Greenstone
R5976	about 22°N	.7045	Greenstone
R5977	about 22°N	.7031	Greenstone
	Average	.7037	
R5978	22°56'N 46°35'W	.7055(1)	Basalt
R5979	22°56'N 46°35'W	.7061(1)	Basalt
R5980	22°56'N 46°35'W	.7065(1)	Basalt

N Normalized to 86/88 = .1194

C Calculated

1 These samples were taken from different portions (see text) of the basalt boulder described by Ciffelli, (1965) and Nicholls, et al, (1964).

2 Figures in parentheses indicate number of analyses.

Table 9

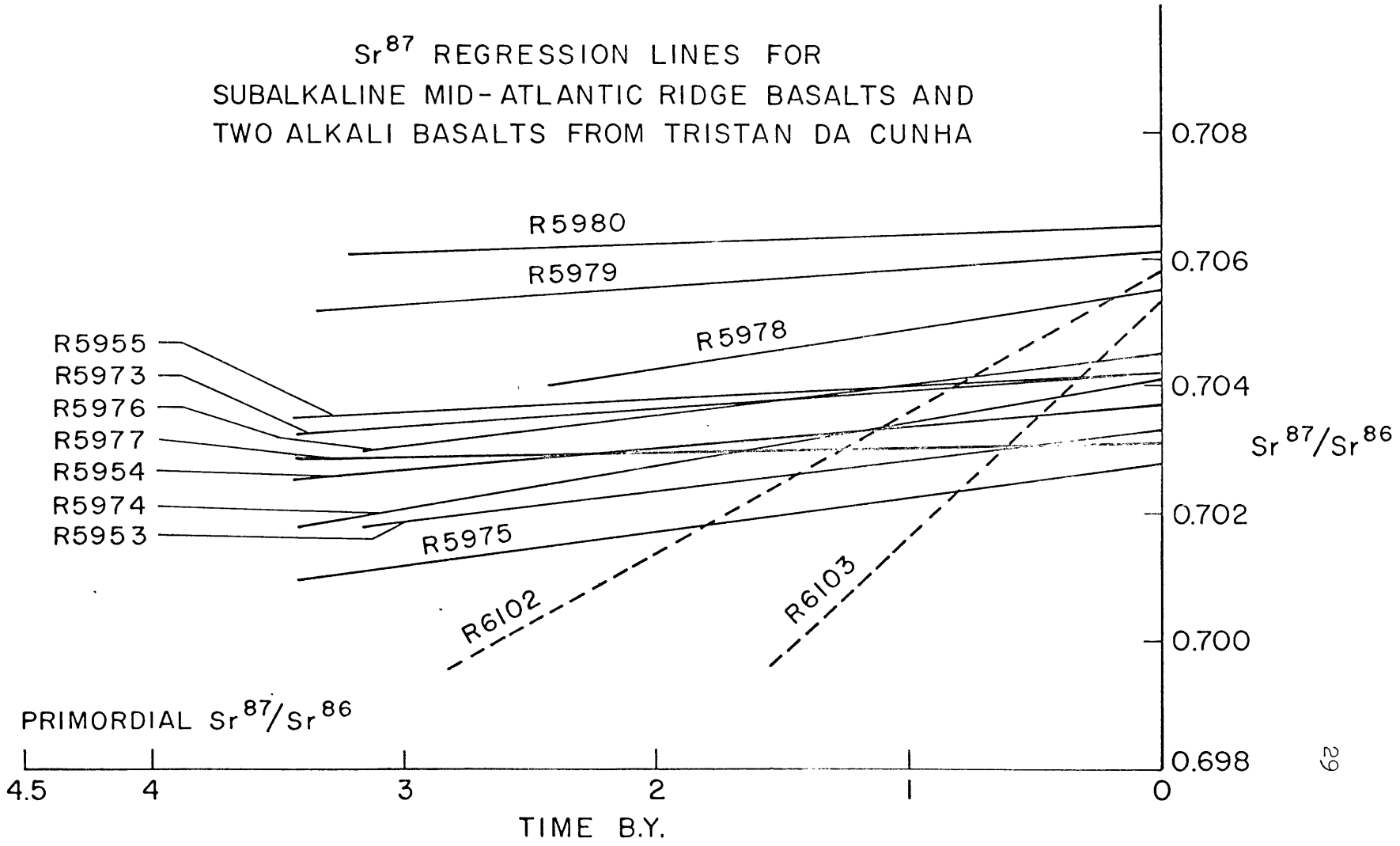
Potassium, Rubidium and Strontium Abundances in Mid-Atlantic Ridge Dredge Samples

Sample No.	K_2O%	Kppm	Rbppm[1]	Srppm	Rb/Sr	K/Rb
R5953	.24	1990	1.47	135.7	.0108	1355
R5954	.08	664	1.19	155.7	.0077	558
R5955	.21	1740	0.51	121.9	.0042	3415
R5973	.14	1160	0.66	101.2	.0065	1760
R5974	.25	2075	2.10	135.8	.0155	1010
R5975	.21	1740	1.57	137.2	.0114	1110
R5976	.08	664	0.21	184.1	.0011	3160
R5977	.05	415	0.15	138.2	.0011	2765
		Avg.	0.98	138.7	.0073	
Basalt Boulder						
R5978			2.52	193.7	.0132	
R5979			1.52	238.0	.0064	
R5980	.13	1080	1.28	348.0	.0037	847

[1]Corrected for Rb blank .048 ppm

FIGURE 3

Sr^{87} Regression Lines for Subalkaline Mid-Atlantic Ridge Basalts and Two Alkali Basalts from Tristan da Cunha


Sr87 REGRESSION LINES FOR
SUBALKALINE MID-ATLANTIC RIDGE BASALTS AND
TWO ALKALI BASALTS FROM TRISTAN DA CUNHA
R5980
R5979
R5978
R5955
R5973
R5976
R5977
R5954
R5974
R5953
R5975
R6102
R6103
0.708
0.706
0.704
0.702
0.700
0.698
Sr87/Sr86
PRIMORDIAL Sr87/Sr86
4.5
4
3
2
1
0
TIME B.Y.

Canary Islands and Madeira

Seven alkaline basalts from the Canary Islands and Madeira, selected on the basis of variability of Rb/Sr ratios, have remarkably consistent Sr^{87}/Sr^{86} ratios (.7032 to .7039 averaging .7035)(Table 10). The abundances of strontium and rubidium vary from about 650 to 1200 and 20 to 80 respectively. With one exception, the Rb/Sr ratios are from .025 to .035 (Table 10). Both strontium and rubidium are enriched in these basalts when compared with the subalkaline basalts of the mid-Atlantic Ridge. Rubidium, however, is enriched to a greater degree than strontium.

The Sr^{87} regression lines for these samples (Figure 4) fan out on both sides of the primordial Sr^{87}/Sr^{86} ratio at 4.5 billion years.

It is important to note that the average Sr^{87}/Sr^{86} ratio for the Canary basalts is similar to the average obtained for the subalkaline oceanic basalts.

Tristan da Cunha

A trachyandesite and a leucite trachybasalt from Tristan da Cunha have Sr^{87}/Sr^{86} ratios of .7053 and .7058 respectively (Table 10). Both rocks are greatly enriched in both rubidium and strontium in comparison with the subalkaline ridge basalts although rubidium is significantly more enriched in late magmatic differentiates. Both Sr^{87} regression lines (Figure 3)

Table 10 Atlantic Ocean Islands

Tristan da Cunha

Sample No.	Name	Sr^{87}/Sr^{86} N	Kppm	Rbppm	Srppm	Rb/Sr	K/Rb
R6102	Leucite trachybasalt	.7058	2820	90	1806	.050	313
R6103	Trachybasalt	.7053	4175	121	1481	.082	345
	Average	.7055					

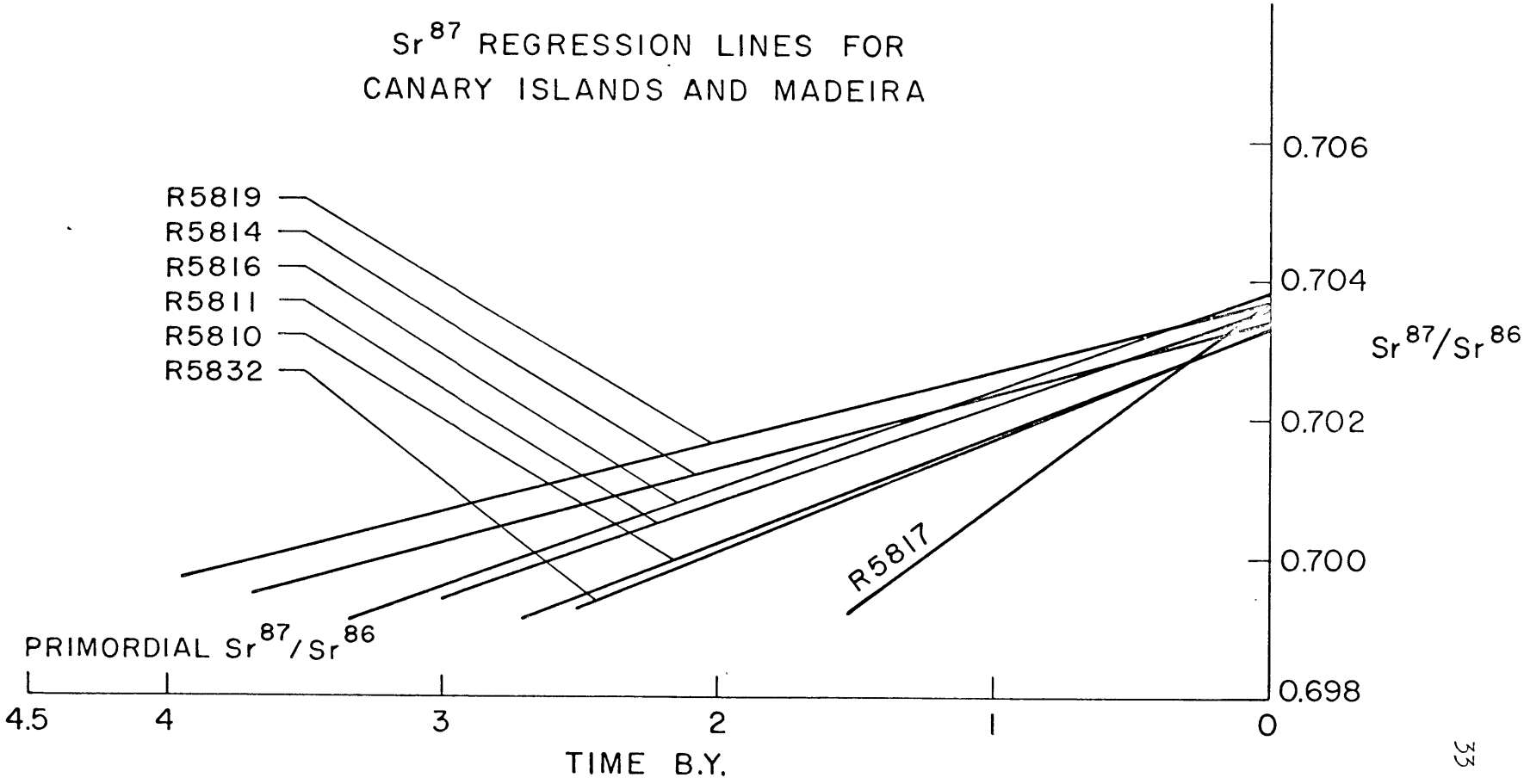
Canary Islands and Madeira

Sample No.	Island	Sr^{87}/Sr^{86} N	Rbppm	Srppm	Rb/Sr
R5810	Hierro	.7032*	36.1	1078	.034
R5811	Hierro	.7036*	25.5	812	.031
R5814	Gomera	.7034*	17.4	739	.024
R5816	Gomera	.7037*	21.2	682	.031
R5817	Teneriffe	.7039*	79.4	1222	.066
R5819	Teneriffe	.7037*	25.4	1146	.022
R5832	Madeira	.7032*	23.3	640	.036
	Average	.7035			

N Normalized to $Sr^{86}/Sr^{88} = .1194$ *Measured Sr^{87}/Sr^{86} ratios

FIGURE 4

Sr^{87} Regression Lines for Canary Islands and Madeira


Sr87 REGRESSION LINES FOR
CANARY ISLANDS AND MADEIRA
R5819
R5814
R5816
R5811
R5810
R5832
R5817
0.706
0.704
0.702
0.700
0.698
Sr87/Sr86
PRIMORDIAL Sr87/Sr86
4.5
4
3
2
1
0
TIME B.Y.

fall considerably short of 4.5 billion years.

From the recent ages of these samples it is apparent that the high Sr^{87}/Sr^{86} ratios are due not to rubidium decay subsequent to basalt formation, but to rubidium concentration relative to strontium in the source region of the upper mantle at an earlier period of earth history. These basalts would have to be at least 300 to 800 million years old for the Sr^{87}/Sr^{86} ratio to have grown from the average oceanic subalkaline basalts to the present value presuming the alkali magma source to have the same isotropic compositions as the subalkaline oceanic basalts.

The strontium isotope data are in close agreement with the results obtained by Gast, Tilton, and Hedge (1964) for Gough Island located 230 miles south-southeast of Tristan da Cunha.

Analyses of a Boulder Dredged from 22°56'N 46°35'W

Samples R5978, R5979, R5980 are from a basalt boulder that is considerably altered. This boulder is a high alumina porphyritic basalt with tholeiitic affinities, described and sketched by Cifelli (1965) with petrographic description and chemical analyses by Nicholls, Nalwalk, and Hays (1964).. R5978 is a sample of the glassy margin, R5979 or an intermediate region, and R5980 of the core. From the high Fe_2O_3/FeO ratio and from the color and opacity of the ground mass, Nicholls, Nalwalk, and Hays (op. cit.) conclude that the groundmass has

experienced considerable alteration, most probably by sea water. The strontium isotope ratios (Table 8) reported here tend to support this conclusion. All three samples have Sr^{87}/Sr^{86} ratios (.7055 - .7066) higher than the highest values yet reported for oceanic dredge samples. Contamination by sea water strontium (Sr^{87}/Sr^{86} = .7090 ± .0005, Faure, et al, 1965; corrected to standard $SrCO_3$ Sr^{87}/Sr^{86} = .7081) can account for these high ratios. The analyses for total strontium and rubidium reveal a pronounced strontium decrease and a very slight rubidium increase from the core to the glassy margin (Table 9). However, because of the porphyritic nature of the sample, it would be a mistake to conclude, just from the rubidium and strontium results, that strontium leaching has occurred. The Sr^{87} regression lines (Figure 3), although displaced slightly from the regression lines for the other mid-Atlantic Ridge samples, do not have significantly different slopes.

The concentration of strontium in the glassy margin of this boulder (R5978) is the same as the average obtained for the other subalkaline basalts from the ridge whereas the interior of the sample (R5980) shows a two- to three-fold enrichment. There is no corresponding enrichment of rubidium.

P. M. Hurley (personal communication) suggests that the enrichment of strontium in the center of the boulder possibly may be due to the distillation of sea water which penetrated the glassy margin while the interior was still hot shortly

after the boulder was erupted. Subsequent leaching of the sea water-introduced strontium could account for the observed strontium concentration gradient.

Pacific Subalkaline Dredge Basalts

Rubidium and strontium abundances and strontium isotopic compositions for three basalts dredged from the East Pacific Rise and four dredged from the Molokai Fracture Zone are reported in Tables 11 and 12.

The Sr^{87}/Sr^{86} ratios for all seven samples are in the range .7027 to .7038 (averaging .7033) which is comparable to the range and average obtained for the mid-Atlantic Ridge samples. The average rubidium and strontium abundances are 2.64 ppm and 123.1 ppm respectively and the average Rb/Sr ratio is .022.

The Molokai samples are much more uniform isotopically and in rubidium and strontium abundances than the East Pacific Rise samples. Admittedly, this may be a sampling feature since the three Rise samples are from widely separated locations whereas the Molokai samples are from a one locality.

Strontium-87 regression lines for these samples are illustrated in Figure 5. With the exception of East Pacific Rise Sample R5951, which has a Rb/Sr ratio of .061, all the regression lines project beyond 4.5 billion years.

The average concentrations of strontium in these basalts is 123.1 ppm and of rubidium, 2.641 ppm.

Table 11

Strontium Isotopic Composition of East Pacific Rise and Molokai Fracture Zone Samples

Sample No.	$Sr^{87}/Sr^{86}\|^{N}_{C}$	$Sr^{87}/Sr^{86}\|^{N}_{M}$	Final $Sr^{87}/Sr^{86}\|^{N}$[1]
East Pacific Rise			
R5950	.7027(2)[2]		.7027
R5951	.7036		.7036
R5952	.7035		.7035
Molokai Fracture Zone			
R5964	.7034(2)[2]	.7034	.7034
R5965		.7033	.7033
R5966	.7039	.7032(C)[3]	.7032
		.7031(S)[3]	
R R5967	.7048(2)[2]	.7039(C)[3]	.7038
		.7036(S)[3]	
		Average	.7033

N Normalized to Sr^{86}/Sr^{88} = .1194

C Calculated ratio

M Measured ratio

1 All $Sr^{87}/Sr^{86}\|^{N}$ ratios corrected to E and A standard $SrCO_3$ = .7081

2 Numbers in parentheses indicate number of analyses

3 Letters in parentheses indicate mass spectrometer used:

(C) Connie

(S) Sally

Table 12

Strontium and Rubidium Concentrations in East Pacific Rise and Molokai Fracture Zone Basalts

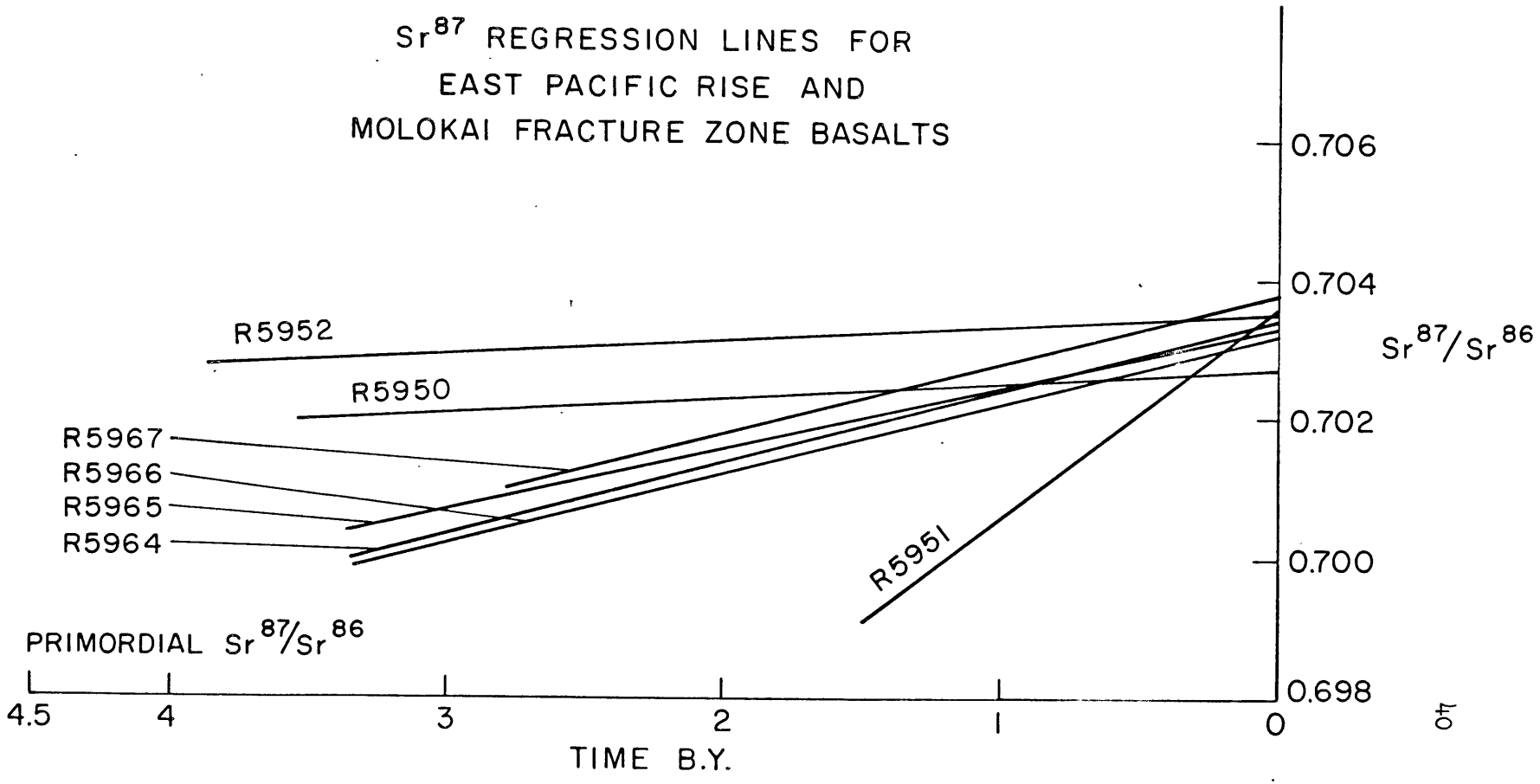
Sample No.	Sr ppm		Rb ppm[1]		Rb/Sr
East Pacific Rise					
R5950	113.3 114.3	> 113.8	0.41		.0036
R5951	110.5		6.77		.0612
R5952	140.7		0.69		.0049
Molokai Fracture Zone					
R5964	114.3 115.2	> 114.8	2.50 2.46	> 2.48	.0016
R5965	132.8 133.2	> 133.0	2.61 2.61	> 2.61	.0196
R5966	122.0 121.5	> 121.8	2.65 2.62 2.67	2.64	.0217
R5967	128.3 126.0	> 127.2	2.87 2.90	> 2.88	.0227
Average	123.1 ppm		2.64 ppm		.0222

[1]Corrected for blank contamination .048 ppm

FIGURE 5

Sr^{87} Regression Lines for East Pacific Rise and

Molokai Fracture Zone Basalts


Sr87 REGRESSION LINES FOR
EAST PACIFIC RISE AND
MOLOKAI FRACTURE ZONE BASALTS
0.706
0.704
0.702
0.700
0.698
Sr87/Sr86
R5952
R5950
R5967
R5966
R5965
R5964
R5951
PRIMORDIAL Sr87/Sr86
4.5
4
3
2
1
0
TIME B.Y.
40

Hawaiian Islands

Eighteen samples representative of the many basalt types found in the Hawaiian Islands have Sr^{87}/Sr^{86} ratios in the range .7027 to .7048 (Table 13). Their rubidium and strontium concentrations, as well as the potassium abundances calculated from the chemical analyses, are reported in Table 14.

On the basis of the Sr^{87}/Sr^{86} ratios, the basalts may be divided into three groups:

1. The tholeiites, characterized by high Sr^{87}/Sr^{86} ratios. They range from .7038 to .7048 and average .7045.
2. The nepheline melilite basalts, which with one exception, tend to have low Sr^{87}/Sr^{86} ratios (.7027 - .7030).
3. The alkali series basalts include the trachyte. Their Sr^{87}/Sr^{86} ratios range from .7028 to .7046.

A correlation of Rb-Sr and La abundances (Schilling and Bence, 1966) also outlines these groups with the exception that the trachyte is placed in a fourth group. These groupings tend to support the conclusion by Powell, et al (1965) that there is a slight but significant decrease of radiogenic Sr^{87} with decreasing silica content. This may be due to a decreasing Rb/Sr ratio with depth in the source region.

Strontium-87 regression lines for the Hawaiian basalts are illustrated in (Figures 6, 7, and 8). The tholeiitic

Table 13

Strontium Isotopic Composition of Hawaiian Basalts

Sample Number		$Sr^{87}/Sr^{86}\Big\|^{N}_{C}$	Sr^{87}/Sr^{86} [1]
R6321	Hawaiite	.7035	.7043(2)
R6322	Basanitoid	.7028	.7033(2)
R6323	Tholeiite	.7038	.7040(2)
R6324	Nepheline basalt	.7030	.7031(3)
R6325	Alkaline-olivine basalt	.7030	.7040(2)
R6326	Trachyte	.7033	.7043(2)
R6327	Melilite-nepheline basalt	.7027(2) [2]	.7030(2)
R6328	Tholeiite	.7048	
R6329	Nepheline-melilite basalt	.7043(2)	
R6330	Linosaite	.7037	
R6331	Nepheline basanite	.7035	
R6332	Ankaramite	.7040	
R6333	Hawaiite	.7044	
R6334	Mugearite	.7046	
R6335	Andesite	.7031	
R6336	Tholeiite	.7048	
R6337	Diabase	.7043	
R6338	Tholeiite	.7046	

[1] Data from Powell, et al (1965) relative to standard $Sr^{87}/Sr^{86} = .7085$

[2] Figures in parentheses indicate number of analyses

[N] Normalized to 86/88 = .1194

[C] Calculated ratio.

Table 14

Strontium and Rubidium Concentrations of Hawaiian Basalts

Sample Number	K ppm*	Sr ppm	Rb ppm	Rb/Sr	K/Rb
R6321	15100	1260	36.6	.029	413
R6322	4980	539	20.6	.038	242
R6323	3070	290	5.73[1]	.020	536
R6324	9960	1303	36.2	.028	275
R6325	6970	419	21.4	.051	326
R6326	40900	54.5	113.8	2.09	359
R6327	14780	1759	46.5	.038	318
		1746 >	46.7 >	.037	
R6328	1245	329	2.18[1]	.007	572
R6329	7550	2155	20.9	.010	361
		2145 >			
R6330	8460	992	28.9	.029	293
R6331	7720	635	22.9	.036	337
R6332	3480	453	16.3	.036	214
R6333	13280	1107	40.2	.036	331
R6334	22580	1061	58.4	.055	387
R6335	10790	908	28.3	.031	381
R6336	1826	396	.495[1] .504[1] .463[1]	.001	3749
R6335	4980	346	5.99[1]	.017	830
R6338	2905	432	6.43[1]	.015	452

*Calculated from chemical analyses

[1]Corrected for rubidium blank contamination .048 ppm

FIGURE 6

Sr^{87} Regression Lines for Hawaiian Tholeiitic Basalts

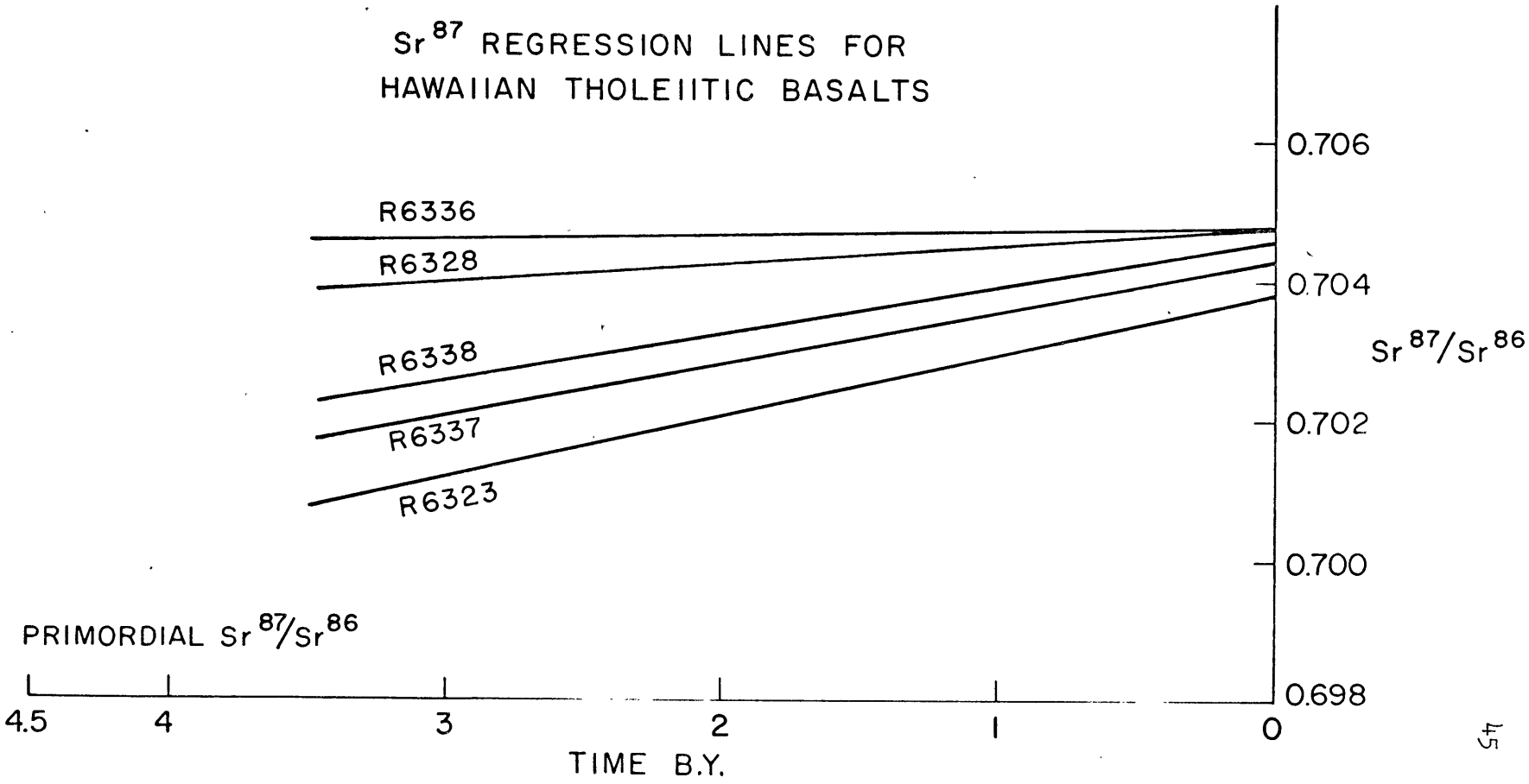

Sr 87 REGRESSION LINES FOR
HAWAIIAN THOLEIITIC BASALTS
R6336
R6328
R6338
R6337
R6323
0.706
0.704
0.702
0.700
0.698
Sr 87/Sr 86
PRIMORDIAL Sr 87/Sr 86
4.5
4
3
2
1
0
TIME B.Y.

FIGURE 7

Sr^{87} Regression Lines for Hawaiian Alkali Series Basalts

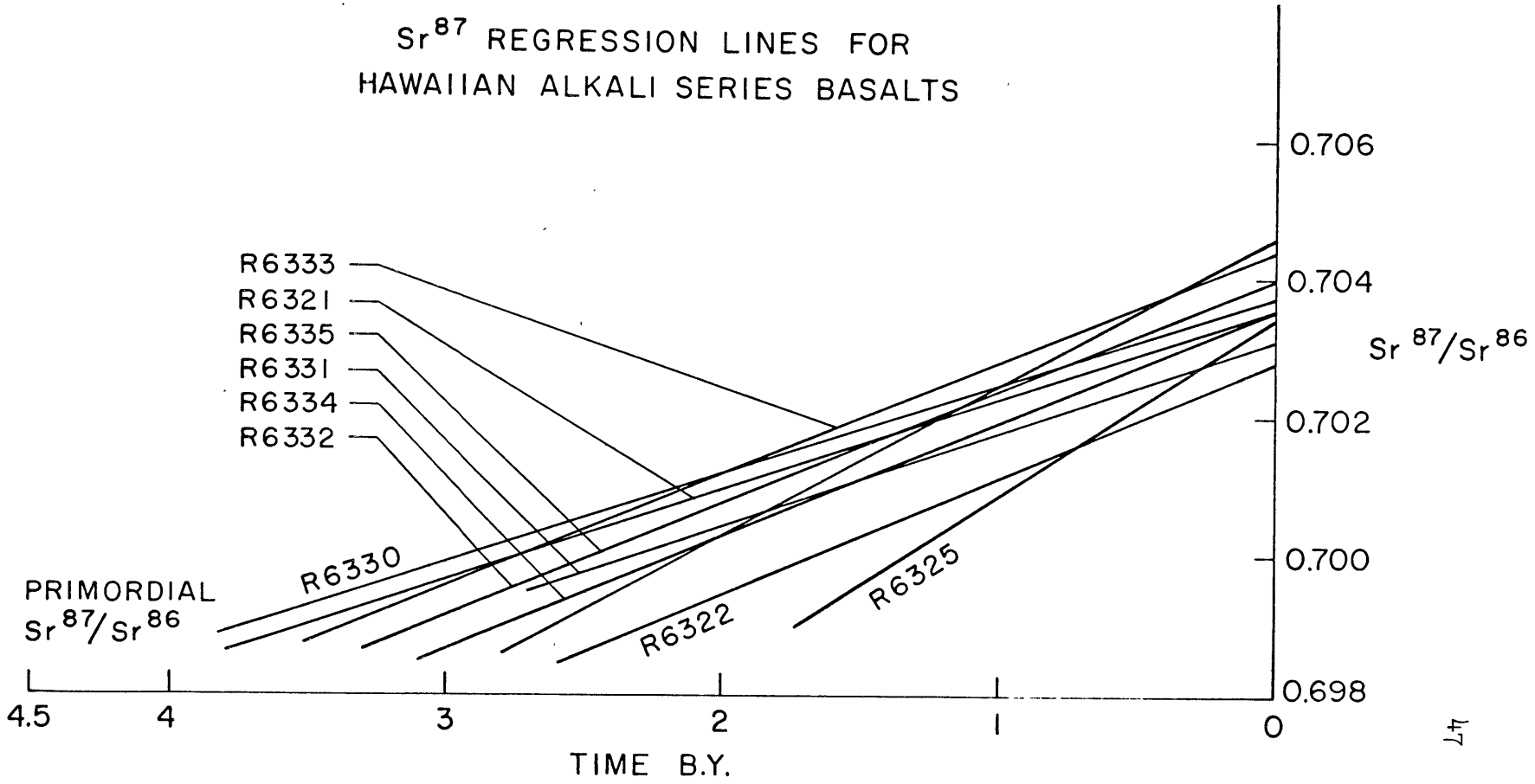
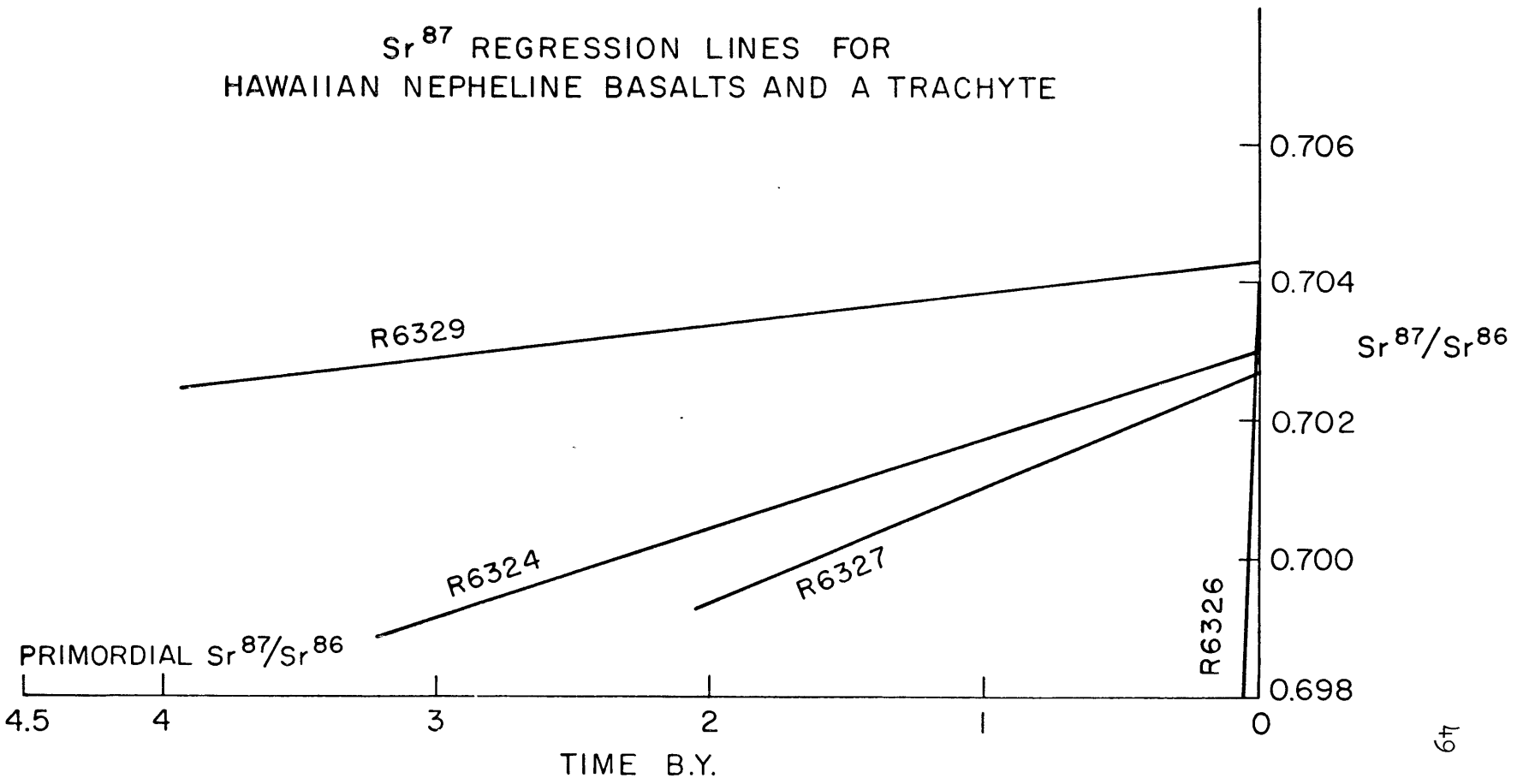

Sr87 REGRESSION LINES FOR
HAWAIIAN ALKALI SERIES BASALTS
R6333
R6321
R6335
R6331
R6334
R6332
R6330
R6322
R6325
PRIMORDIAL
Sr87/Sr86
0.706
0.704
0.702
0.700
0.698
Sr 87/Sr 86
4.5
4
3
2
1
0
TIME B.Y.

FIGURE 8

Sr^{87} Regression Lines for Hawaiian Nepheline Basalts

and a Trachyte


Sr 87 REGRESSION LINES FOR
HAWAIIAN NEPHELINE BASALTS AND A TRACHYTE
0.706
0.704
0.702
0.700
0.698
Sr 87/Sr 86
R6329
R6324
R6327
R6326
PRIMORDIAL Sr 87/Sr 86
4.5
4
3
2
1
0
TIME B.Y.

basalts, like the subalkaline basalts from the oceanic ridges, extend back beyond 4.5 billion years. All the other samples extend back to 4.5 billion years or fall short of it. The rubidium enrichment in the trachyte, relative to strontium, is so great that the regression line slope is approaching infinity.

It is important to note that the Hawaiian tholeiites have about a three-fold enrichment in both strontium and rubidium over the subalkaline ridge basalts although the Rb/Sr ratios are almost identical. The Sr^{87}/Sr^{86} ratios for the Hawaiian tholeiites as a group are consistently higher than the same ratio for the subalkaline ridge basalts.

With one exception, the K/Rb ratios (Table 14) for the Hawaiian tholeiites occur in the range 450 to 800 and are all lower than the K/Rb ratios in the subalkaline dredge basalts. The exception, R6336 has an unusually high K/Rb ratio due to an extremely small rubidium concentration.

The K/Rb ratios for the alkali and nepheline-bearing series lie in the range from about 250 to 400 with an average of 326. There is no systemmatic decrease of K/Rb ratios with increasing K_2O.

Summary

A number of important observations can be made from the results of this investigation.

1. The subalkaline basalts dredged from the ocean floors and ridges have low concentrations of rubidium and strontium in comparison with the subalkaline and alkaline island basalts. The subalkaline island basalts such as the Hawaiian tholeiites have a two- to three-fold enrichment of both rubidium and strontium over their ocean floor and ridge counterparts.
2. The Rb/Sr ratios for the subalkaline basalts (island and ridge) are low (about .01) and, when the Sr^{87} regression lines are drawn, they project back beyond 4.5 billion years at the primordial Sr^{87}/Sr^{86} ratio.
3. The oceanic alkaline basalts are all enriched in rubidium relative to strontium such that their Rb/Sr ratios are considerably greater than for the subalkaline basalts. The Sr^{87} regression lines for the alkaline basalts fall short of 4.5 billion years at the primordial Sr^{87}/Sr^{86} ratio.
4. The Sr^{87}/Sr^{86} ratios for all fresh oceanic basalts occur in the range .702 to .706 with the following averages noted for the localities sampled (number of analyses in parentheses):

East Pacific Rise and Molokai Fracture Zone	.7033(7)
Mid-Atlantic Ridge	.7037(8)

Canary Islands and Madeira	.7037(7)
Tristan da Cunha	.7055(2)
Hawaiian Islands	.7038(18)

5. The Hawaiian basalts may be divided into three groups on the basis of their Sr^{87}/Sr^{86} ratios:

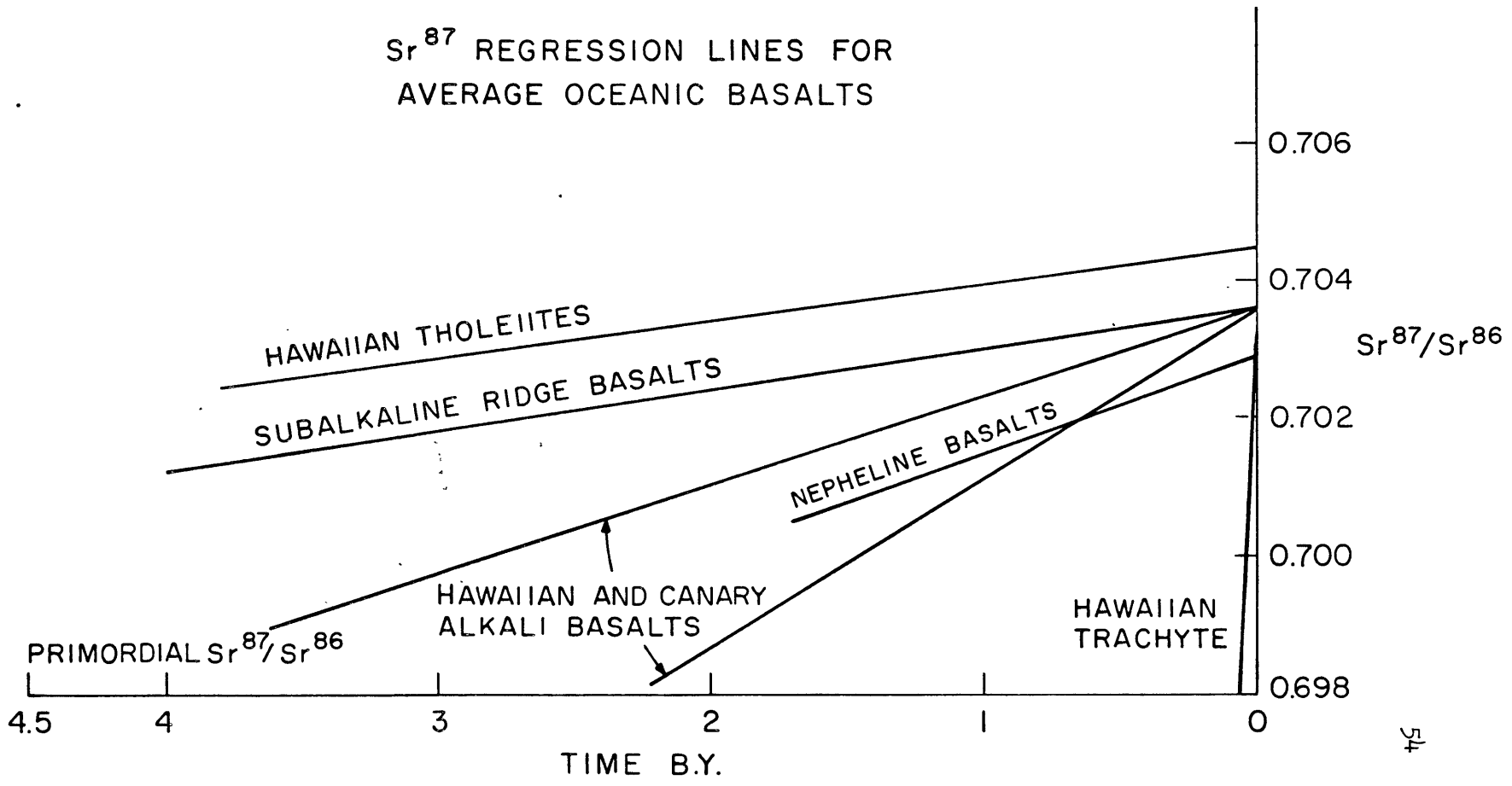
a) Tholeiites	.7045(5)
b) Nepheline melilite basalts	.7029(2)
c) Alkaline series and trachyte	.7036(10)

6. The K/Rb ratios for the subalkaline dredge basalts are variable, but in the range 550 to 3400 and are the highest of any terrestrial materials. The subalkaline basalts from the Hawaiian Islands, have with one exception, K/Rb ratios from 450 to 800. The alkaline basalts from the Hawaiian Islands and Tristan da Cunha have K/Rb ratios from 250 to 400. No systematic decrease of K/Rb ratios with increasing K_2O is noted in the alkaline basalts from the Hawaiian Islands.

A summary of the rubidium-strontium relationships in the samples is shown on the Sr^{87} regression diagram of Figure 9.

FIGURE 9

Sr^{87} Regression Lines for Average Oceanic Basalts


Sr^{87} REGRESSION LINES FOR
AVERAGE OCEANIC BASALTS
HAWAIIAN THOLEIITES
SUBALKALINE RIDGE BASALTS
NEPHELINE BASALTS
HAWAIIAN AND CANARY
ALKALI BASALTS
HAWAIIAN
TRACHYTE
PRIMORDIAL Sr^{87}/Sr^{86}
0.706
0.704
0.702
0.700
0.698
Sr^{87}/Sr^{86}
4.5
4
3
2
1
0
TIME B.Y.

DISCUSSION AND CONCLUSIONS

The oceanic basalts analyzed in this study and elsewhere (Faure and Hurley, 1963; Hedge and Walthall, 1963; Lessing and Catanzaro, 1964; Gast, Tilton, and Hedge, 1964; Hamilton, 1965a,b; McDougall and Compston, 1965; Moorbath and Walker, 1965; Powell, Faure, and Hurley, 1965; Tatsumoto, Hedge, and Engel, 1965; and Pushkar, 1966) have Sr^{87}/Sr^{86} ratios that fall within a very narrow range (.702 to .705) with minor exceptions. This indicates that the upper mantle source regions for these basalts must have been uniform with respect to their Rb/Sr ratio for much of the earth's history.

On the other hand, variations in the Sr^{87}/Sr^{86} and lead isotope ratios for recent oceanic alkali basalts from widely separated localities (Gast, Tilton, and Hedge, 1964; Tatsumoto, 1966; this study) indicate that Rb/Sr and U/Pb heterogeneities were developed on a regional scale in the upper mantle early in the earth's development.

From the results of this investigation, it is seen that subalkaline oceanic basalts dredged from the mid-oceanic ridges are characterized by uniformly low abundances of both rubidium and strontium and very low (for basalts) Rb/Sr ratios (about .01). The average Sr^{87}/Sr^{86} ratio obtained for these subalkaline basalts is about .703, much too high to have been generated from material having a Rb/Sr ratio of .01 and an initial Sr^{87}/Sr^{86} ratio of

.698. Evidently, the source material from which these basalts were derived had a higher Rb/Sr ratio in order to develop the necessary radiogenic Sr^{87}.

If strontium was "enriched" relative to rubidium, and that is the case here even though the abundances of both elements are low, one of two situations must have prevailed. The strontium "enriched" system must have been residual in nature, or the partitioning behavior of rubidium and strontium between the basalt magma and coexisting solid phases must have changed drastically. In view of our present knowledge of the behavior of trace elements, the concentration of strontium over rubidium in a liquid phase, which is either residual from fractional crystallization of a melt or a differentiate of partial melting, seems unlikely. It seems most probable, therefore, that the subalkaline oceanic basalt mamgmas have passed through a residual stage in their development.

The possibility that subalkaline basalt magmas were derivatives of a basic residual layer in the upper mantle previously suggested by Tatsumoto (1966) is further substantiated here. It does not appear reasonable, to this investigator, that the subalkaline oceanic basalts were derived by the partial melting of upper mantle material unless the trace components, rubidium in particular, were previously removed. Partial melting without prior removal of rubidium would require two discrete periods of melting for the production of subalkaline magmas; one to remove

the alkali components and the second to generate the subalkaline magma. This implies that considerable quantities of alkali- and trace-component-rich basalts were extruded in oceanic areas before subalkaline basalt magmas. This is a reversal of the tholeiite-alkali basalt relationships noted in the Hawaiian Islands.

Therefore, we are still faced with the problem of removing rubidium from the subalkaline basalt magma source regions. To this investigator, the most attractive solution to this problem is the removal of rubidium-enriched liquids, as well as other trace elements, alkalis, and Al_2O_3, from the oceanic upper mantle by continuing convection in an asymmetrically differentiating earth. The asymmetries, now obvious at the surface by the positioning of the continents and ocean basins, and inferred at depth from the heat flow data, may be a direct consequence of the localization of core infall in the earth's very early history in the manner suggested by Elsasser (1963). The implications of this model are discussed in more detail in Part II of this thesis.

In a convecting upper mantle the oceanic regions are unstable due to slow heating from the decay of long-lived radionuclides. Therefore, these regions may become the rising limb of a convection cell. The downsinking limb is located under the continental plates.

Trace elements, alkalis, and alumina in the oceanic upper

mantle are swept to the surface and then outward to the continental areas where, because of their low densities, they are unable to return to the mantle on the downward limb of the convection cell and are added to the continental plates.

Admittedly this model is speculative, however it is becoming increasingly evident that convection currents are distinct possibilities and must be considered as major influencing processes in any earth model.

Conclusions arising from the results of the Rb-Sr analyses of the oceanic basalts are:

1. Oceanic basalt source regions are generally quite uniform with respect to their Rb/Sr ratio but small scale regional Rb/Sr heterogeneities, produced early in the earth's differentiation history, are present.
2. Alkali and subalkaline basalt magmas are derived from similar source material in the upper mantle.
3. The Recent subalkaline basalts forming the ocean floors and ridges were generated by the partial or complete melting of material that had been depleted in rubidium relative to strontium at an earlier stage in the differentiation of the earth.
4. Recent oceanic alkalic and acidic basalts owe their enrichments of rubidium and strontium and their high Rb/Sr ratios (relative to subalkaline basalts) to geologic processes that occurred at the time of their generation or subsequent differentiation.

Although the results of this investigation in themselves do not establish the general history of differentiation in the earth, they add support to a complex development, one that is compatible with an asymmetrical model.

ACKNOWLEDGEMENTS

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PART II

THE DIFFERENTIATION HISTORY OF THE EARTH BY RUBIDIUM-STRONTIUM ISOTOPIC RELATIONSHIPS

CHAPTER I

INTRODUCTION

Statement of the Problem

It is well known that the behavior of trace elements in geological processes is controlled not only by the intrinsic properties of the ions themselves according to the rules first established by Goldschmidt, but also by the physico-chemical conditions of the processes to which they are subjected. Studies of trace element pairs, or better still, groups, in differentiated suites of volcanic rocks enable geochemists to predict the patterns that these elements follow relative to each other during magmatic processes. Once these patterns are established it is possible, by studying the distribution of trace element pairs in a rock, to place certain limitations upon the sequence of events that combined to produce the rock.

Rubidium and strontium prove to be an exceptionally well-adapted pair for determining the evolutionary history of their host rocks. Both are classified as lithophile elements and, because of their large ionic radii (Sr^{++}= 1.18Å and Rb^{+}= 1.47Å) relative to the major rock-forming cations, tend to become concentrated in the liquid fraction of magmatic processes. Of the major rock-forming elements, rubidium replaces only potassium by admission into the potassium minerals. Strontium on the other hand is admitted into calcium-bearing minerals or, to a

smaller degree, is captured by potassium-bearing minerals. This trace element pair is even more valuable as a geochemical tool because, unlike stable element pairs, it introduces the time element into the geochemical evolutionary history of the host rock.

Various lines of evidence point to the upper mantle as being the source region for the oceanic basalts. Therefore, the rubidium and strontium isotopic relationships of these derivative basalts should reflect the rubidium-strontium characteristics of the upper mantle. The key to this problem may be the extensive subalkaline oceanic basalts that occur on the mid-oceanic ridges, along the large fracture zones in the ocean floors, and in the ocean basins. They appear to represent the predominant basalt magma produced in the upper mantle and from chemical criteria, appear to be the most primitive of all basalts. Until very recently, no rubidium-strontium analyses were reported for these basalts and what has become available in the past two years is scanty.

The purpose of this investigation is to obtain more representative rubidium-strontium data for the subalkaline oceanic basalts as well as further determinations for alkalic oceanic basalts and to relate the results to a possible sequence of events in the earth's evolutionary history.

Previous Work

Subalkaline Dredge Basalts. As far back as in the late nineteenth century rock samples were dredged from the ocean floors. The records from these and subsequent expeditions are few and it wasn't until the outbreak of the Second World War that really significant contributions were made in oceanographic research. This research was directed primarily at the physiographic features of the ocean floors.

The physical features of the oceanic ridges and the history and development of the ridges and basins are discussed in the recent literature by Menard (1958; 1964), Hess (1959, 1962, 1965), Heezen, Tharp, and Ewing (1959), Bott (1965), Heirtzler and Le Pichon (1965), van Andel, et al (1965), and Ewing, Le Pichon, and Ewing (1966).

Some of the earliest descriptions and analyses of dredge basalts from the oceanic ridges are reported by Murray and Renard (1891), Correns (1930), Wiseman (1937), and Shand (1949). The surge in oceanographic research in the past decade has lead to more extensive stuides of the heretofore poorly understood subalkaline submarine volcanic rocks of the Atlantic and Pacific mid-ocean ridges and deeps (Quon and Ehlers, 1963; Nicholls, 1965; Engel and Engel, 1964a,b; Muir and Tilley, 1964; Nicholls, Nalwalk, and Hays, 1964), from the ocean floor near Hawaii

(Moore and Reed, 1963; Moore, 1965), and from the floor of the Indian Ocean (Matthews, Vine, and Cann, 1965; Engel, Fisher, and Engel, 1965). Basalts of very similar chemical composition are also found beneath the ocean floor at the experimental Moho site off Guadalupe Island in the eastern Pacific (Engel and Engel, 1961).

Major and minor element analyses of "oceanic tholeiites" from the mid-Atlantic Ridge and East Pacific Rise are described in detail by Engel, Engel, and Havens (1965). These basalts are characterized by extremely low amounts of Ba, K, P, Pb, Sr, Th, U, Ti, Rb, and Zr as well as $Fe_2O_3/FeO < 0.2$ and $Na/K > 10$ in unaltered samples. The K/Rb ratios for oceanic tholeiites as reported by Gast (1965) are extremely variable but are all higher than those observed for any other terrestrial material and are more comparable to the calcium-rich achondrites. From the chemical criteria, Engel, et al (1965) suggest that these basalts are a primary and predominant magma erupted from the mantle, and the later, much less voluminous, and stratigraphically higher alkali-rich basalts of the volcanic islands and submarine volcanoes are derivatives of the tholeiites by fractional crystallization.

Recently it has been shown by Melson, et al, (1966) that greenstones occur in the central valley of the mid-Atlantic Ridge. Some of these greenstones are derived from basaltic

flows and others from tuffs. Except for the fact that these greenstones have Fe_2O_3/FeO ratios > .25 they could be classified as "tholeiitic" according to Engel, et als (1965) criteria. Similar but more highly brecciated volcanics are found on the Carlsberg Ridge in the Indian Ocean (Matthews, Vine, and Cann, 1965).

The rare earth patterns obtained for the subalkaline basalts from the oceanic ridges (Frey and Haskin, 1964) show that there is considerable enrichment over the chondrite abundances but that there is no significant fractionation of the light rare earths. This is interpreted as an indication of the primitive origin for these basalts. On the other hand, Schilling and Winchester (1966b) interpret the oceanic tholeiite rare earth patterns as indicating considerable differentiation but with only slight fractionation.

Very few rubidium-strontium analyses of the sub-alkaline oceanic basalts are reported in the literature. Previous to this study, only six analyses are reported. Five of these, two from the East Pacific Rise and three from the mid-Atlantic Ridge, are reported by Tatsumoto, Hedge, and Engel (1965). A single analysis for a mid-Atlantic Ridge sample is reported by Faure and Hurley (1963). The results of these studies are reported in Table 1. Murthy and Steuber (1963) measured the strontium isotopic composition of four recent volcanics from the Pacific Ocean basin and report Sr^{87}/Sr^{86} ratios in the range .705 to .709 $\pm$ .002. East Pacific Rise basalts also analyzed are reported to have the same range.

Table 1

Published Results of Rubidium-Strontium Studies of Subalkaline Oceanic Dredge Basalts

	Locality	$Sr^{87}/Sr^{86}\|^{N}$	Rb ppm*	Sr ppm*	Rb/Sr
Atlantic	20°40'S 13°16'W	.7024[1]	1.14	134	0.0085
	5°47'S 11°25'W	.7027[1]	2.63	109	0.024
	9°39'N 40°27'W	.7021[1]	0.66	150	0.0044
	31°18'N 40°54'W	.7032[2]	9.25	118.3	0.0824
Pacific	12°52'S 110°57'W	.7016[1]	1.06	86	0.012
	18°25'S 113°20'W	.7017[1]	0.45	98	0.0045

*Determined by isotope dilution techniques.

[1]Data from Tatsumoto, Hedge, and Engel (1965). No standard data are given for comparison.

[2]Data from Faure and Hurley (1963) relative to Sr^{87}/Sr^{86} = .7080 for standard $SrCO_3$.

Volcanic Islands. The alkali-rich and subalkaline basalts of the oceanic islands have been more extensively investigated than their submarine counterparts. In particular, the Hawaiian Islands are probably the most carefully studied sequence of oceanic basalts anywhere. Detailed petrologic, petrographic, and petrogenetic relationships of these volcanics (Washington, 1923; Powers, 1935, 1955; Daly, 1944; Stearns, 1946; MacDonald and Powers, 1946; Winchell, 1947; Wentworth and Winchell, 1947; MacDonald, 1949; Tilley and Scoon, 1961; MacDonald and Katsura, 1964) reveal that the subalkaline basalts (tholeiites) and their derivatives form the broad base upon which these shield volcanoes are built and are capped by much smaller amounts of alkaline basalts.

Minor element studies of the Hawaiian Islands volcanic suites are reported by Wager and Mitchell (1953). Potassium-rubidium relationships are discussed by Lessing, Decker, and Reynolds (1963). They interpreted a decreasing K/Rb ratio in response to increasing K_2O as being an indication of the contamination of the original magma by argillaceous sediments.

Strontium isotope analyses reported for the Hawaiian basalts are quite numerous (Hedge and Walthall, 1963; Faure and Hurley, 1963; Lessing and Catanzaro, 1964; Powell, Faure, and Hurley, 1965; Hamilton, 1965a) but of these only the paper by Faure and Hurley (1963) also reported Rb/Sr ratios.

Eight basalt samples of variant chemistry analyzed by Powell, Faure, and Hurley, (1965) show slightly increasing Sr^{87}/Sr^{86} ratios with increasing silica content. Seven of these samples are reanalyzed in the present study with additional determinations of rubidium and strontium concentrations.

The first complete report on the volcanic rocks of Tristan da Cunha, a group of three islands situated astride the mid-Atlantic Ridge in the south Atlantic, is given by Baker, et al (1964). This report was compiled by the expedition of the British Museum to the islands in 1962 following the 1961 eruptions. It includes detailed descriptions of the basalts as well as major and minor element analyses of numerous samples. Emission spectrographic techniques were employed to determine the concentrations of the minor elements. Strontium concentrations in these basalts increase with differentiation until they reach a maximum in the intermediate members and then fall off rapidly in the trachytic rocks. Rubidium increases continually with differentiation although the K/Rb ratio remains relatively constant.

Hamilton (1963) makes fleeting mention of Sr^{87}/Sr^{86} ratios for the Tristan volcanics and gives a preliminary figure of .702. Potassium-argon age determinations for Tristan and for other parts of the mid-Atlantic Ridge are reported by Miller (1964). The Tristan basalts average one million years by the K-Ar techniques, but according to the paleomagnetic data, this appears

to be the age of the oldest exposed basalts. Many of the younger basalts erupted in Recent time. Two submarine alkali basalts, one from the Discovery sea mount (42°03.9'S 0°03.5'E) and one from the mid-Atlantic Ridge (27°43'W 45°44'N) gave K-Ar ages Of 26 $\pm$ 4 and 29 $\pm$ 4 million years respectively.

Strontium isotope analyses for volcanic rocks from the islands along the Ridge are reported in the literature. Gast, Tilton, and Hedge (1964) analyzed the basalts of Gough and Ascension Islands for both strontium and lead isotopes and noted a peculiar reversal in the concentrations of radiogenic lead and strontium between the two localities. The average Sr^{87}/Sr^{86} ratio for the basalts of Gough Island is .7026 and for Ascension, .7053. The lead data, on the other hand, show that the Gough basalts are more radiogenic than those from Ascension. These differences are interpreted as an indication of regional variations in the U/Pb and Rb/Sr ratios in the upper mantle source regions of these basalts.

A single strontium isotope analysis for the Azores is reported by Faure and Hurley (1963). The Sr^{87}/Sr^{86} ratio for this basalt (corrected to the standard $SrCO_3$ = .7080) is .7058.

Moorbath and Walker (1965) analyzed an extensive suite of Icelandic volcanics having compositions varying from tholeiitic to acidic and found very low sr^{87}/Sr^{86} ratios for all types.

The average Sr^{87}/Sr^{86} ratio for 19 samples is .7026 which agrees with the .7025 obtained by Hedge and Walthall for two Icelandic basalts. Moorbath and Walker (1965) interpret the similarity in Sr^{87}/Sr^{86} ratios between the basic and acidic volcanics on Iceland as an indication that both types are derivatives of the same upper mantle source region.

Pushkar (1966) determined Sr^{87}/Sr^{86} ratios for recent volcanic rocks in the island arcs of the Lesser Antilles and western Pacific Ocean. The volcanic rocks from the Northern Mariana and Izu Islands have Sr^{87}/Sr^{86} ratios of about .7040 whereas the Lesser Antilles volcanics vary from .7040 to .7090 in strontium isotopic composition. Pushkar concludes that the former group are relatively uncontaminated derivatives of the upper mantle while the latter may have undergone varying degrees of contamination by ocean sediments whose strontium is in equilibrium with sea water strontium.

Hamilton (1965b) and McDougall and Compston (1965) measured the isotopic composition of strontium in the alkaline and subalkaline volcanics of Reunion and Rodriguez Islands in the Indian Ocean. The average Sr^{87}/Sr^{86} ratio for these basalts is about .7040. McDougall and Compston (1965) also determined potassium and rubidium abundances in these basalts.

Alpine-type Ultramafics. In recent years, trace element research applied to the history and origin of basalts has also focused on the alpine-type untramafics which are presumed to be the residual fraction remaining in the continental upper mantle following derivation of the basalt magma. Two different interpretations of the Sr^{87}/Sr^{86} and Rb/Sr ratios arose from these investigations. Steuber and Murthy (1966b) on the basis of high Sr^{87}/Sr^{86} ratios (about .71) and low Rb/Sr ratios (about .01) conclude that the alpine-type ultramafics appear to be "residual in nature and can be neither the source material for the derivation of basalts nor the refractory residue of modern basalts". Roe (1964), although he obtained similar Sr^{87}/Sr^{86} ratios, found considerably higher Rb/Sr ratios, and concluded that the alpine-type ultramafics were the residual material left behind in the upper mantle following the removal of a basaltic liquid phase. The difference in Rb/Sr ratios in these two studies is due to a factor of ten difference in the strontium concentrations. There are, however, similarities in the rubidium concentrations. A reanalysis of the Dun Mountain, New Zealand, dunite, the only locality sampled both by Roe (1964) and Steuber and Murthy (1966b), is reported in Appendix B.

Potassium-rubidium relationships in the ultramafic[78] rocks are reported by Steuber and Murthy (1966a). The low K/Rb ratios (200-500) are interpreted as an indication that the alpine-type ultramafics are residuals from an alkali-enriched upper mantle.

Theory of Rubidium-Strontium Isotopic Evolution

General relationships. Details of the theory of the Rb-Sr age-dating method are discussed by Compston and Jeffrey (1959), Schreiner (1958), Allsopp (1961), recently reviewed by Lanphere, Wasserburg, Albee, and Tilton (1964). A brief review is warranted here.

Naturally occurring rubidium has two isotopes, Rb^{85} and Rb^{87}. The former is neither radioactive nor the radiogenic daughter product of a naturally occurring radioactive species. The latter decays by β-emission to Sr^{87} with a half-life of approximately 50 billion years which is long compared to the age of the earth. Natural strontium has four stable, non-radiogenic isotopes, Sr^{84}, Sr^{86}, Sr^{87}, and Sr^{88}, and the radiogenic daughter of Rb^{87} decay, Sr^{87*}. In any system that has remained chemically closed with respect to rubidium and strontium, the abundance of Sr^{87} at any time "t" is the initial Sr^{87} abundance, $\left[Sr^{87}\right]_o$, determined at the time the system last became closed, plus the time integrated result of Rb^{87} decay (Sr^{87*}). The

algebraic expression for this relationship is:

$$Sr^{87}\Big]_t = Sr^{87}\Big]_o + Sr^{87*} \qquad (1)$$

The basic decay equation for radioactive decay is

$$\frac{dN}{dt} = -\lambda N \ , \qquad (2)$$

integrating and substituting for Rb^{87} and Sr^{87*} gives

$$Sr^{87*} = Rb^{87}(e^{\lambda t} - 1) \qquad (3)$$

By substitution in Equation 1 and dividing by Sr^{86} which does not change with time, the following relationship is obtained;

$$Sr^{87}/Sr^{86}\Big]_t = Sr^{87}/Sr^{86}\Big]_o + Rb^{87}/Sr^{86}\Big]_t (e^{\lambda t} - 1) \qquad (4)$$

Where: t = age of system in years

λ = the decay constant for Rb^{87} in reciprocal years

$Sr^{87}/Sr^{86}\Big]_t$ = atomic ratio of Sr^{87} to Sr^{86} at t years following the last closure of the system (t = present time).

$Sr^{87}/Sr^{86}\Big]_o$ = atomic ratio of Sr^{87}/Sr^{86} at instant system became closed (t = 0).

$Rb^{87}/Sr^{86}\Big]_t$ = atomic ratio of Rb^{87} to Sr^{86} at t years following last closure of the system (t = present time).

Considerable controversy has arisen concerning the exact value of the decay constant for Rb^{87}. This is due primarily to the difficulty in measuring it precisely with β-counting techniques. However, in keeping with the practice of the majority of laboratories, the value of 1.39×10^{-11} $years^{-1}$ (Aldrich, et al, 1956) is used here. This number was established by comparison with U-Pb ages. The subject of the Rb^{87} half-life is recently reviewed by Leutz, Wenninger, and Ziegler (1962).

For age-dating purposes, equation (3) cannot be solved as it stands since two unknowns are involved, t and $Sr^{87}/Sr^{86}\Big]_o$. This difficulty is circumvented if the chemical system under consideration is composed of a number of subsystems which became closed at the same time as the major system. An equation similar to (3) is written for each subsystem:

$$Sr^{87}/Sr^{86}\Big]_t^1 = Sr^{87}/Sr^{86}\Big]_o^1 + Rb^{87}/Sr^{86}\Big]_t^1 (e^{\lambda t}-1) \text{ subsystem (1)} \quad (5)$$

$$Sr^{87}/Sr^{86}\Big]_t^2 = Sr^{87}/Sr^{86}\Big]_o^2 + Rb^{87}/Sr^{86}\Big]_t^2 (e^{\lambda t}-1) \text{ subsystem (2)} \quad (6)$$

Assuming that strontium was isotopically homogeneous at time zero, the $Sr^{87}/Sr^{86}\Big]_o$ ratio for each subsystem is identical, and equations (4) and (5) can be solved simultaneously. Providing

the assumptions of closed systems are valid, three or more subsystems of closed systems are valid, three or more subsystems plotted on a graph with $Rb^{87}/Sr^{86}\Big]_t$ as ordinate and $Sr^{87}/Sr^{86}\Big]_t$ as abscissa fall on a straight line or "isochron". This concept was introduced by Nicolaysen (1961). The $Sr^{87}/Sr^{86}\Big]_o$ ratio for the system is determined from the point of intersection of the isochron with the abscissa and the time at which the major system and subsystems became closed is determined from the slope ($\tan \theta$) of the isochron where

$$\tan \theta = e^{\lambda t} - 1 \qquad (7)$$

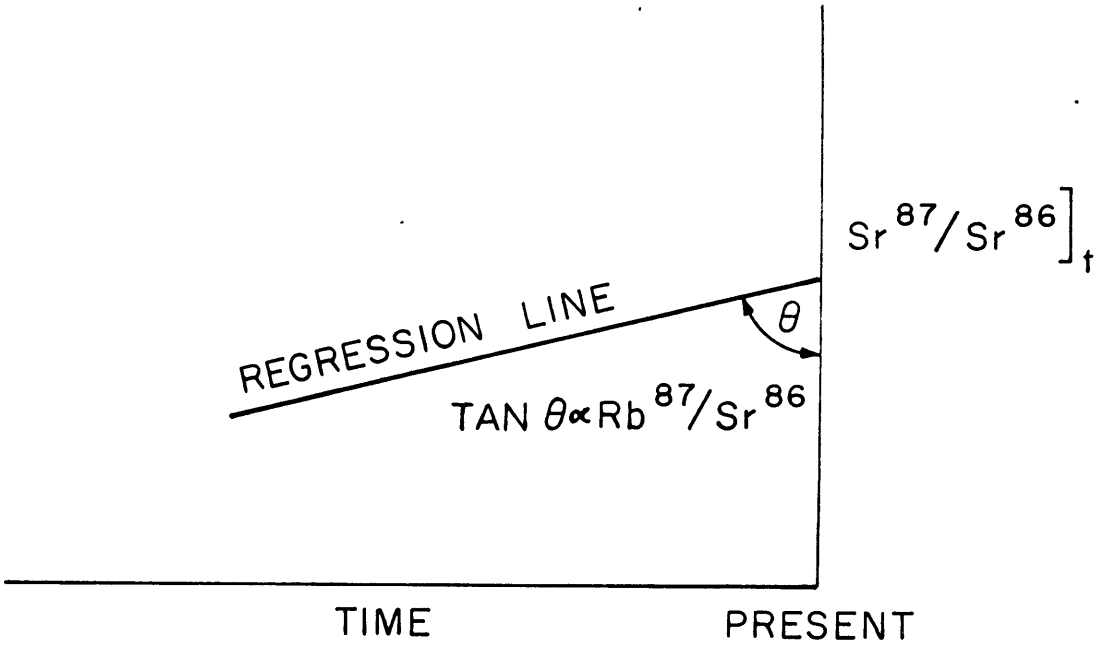
Regression Lines. Because the abundance of Sr^{87}, generally expressed in terms of Sr^{87}/Sr^{86} ratios, increases at a rate dependent upon the abundance of Rb^{87} associated with it, it is possible to determine the characteristics of the development of Sr^{87}/Sr^{86} in the last evolutionary stage of any rock from its observed Rb/Sr and Sr^{87}/Sr^{86} ratios. This "evolution" of Sr^{87}/Sr^{86} for any given Rb/Sr ratio is expressed graphically as a function of time by a regression plot (Figure 1). The ratio $Sr^{87}/Sr^{86}\Big]_{observed}$ is plotted as the ordinate and time from zero to 4.5 b.y. as the abscissa. The slope of the regression line is proportional to the Rb^{87}/Sr^{86} ratio. A practical example of regression diagrams is the determination of the time at which a

FIGURE 1

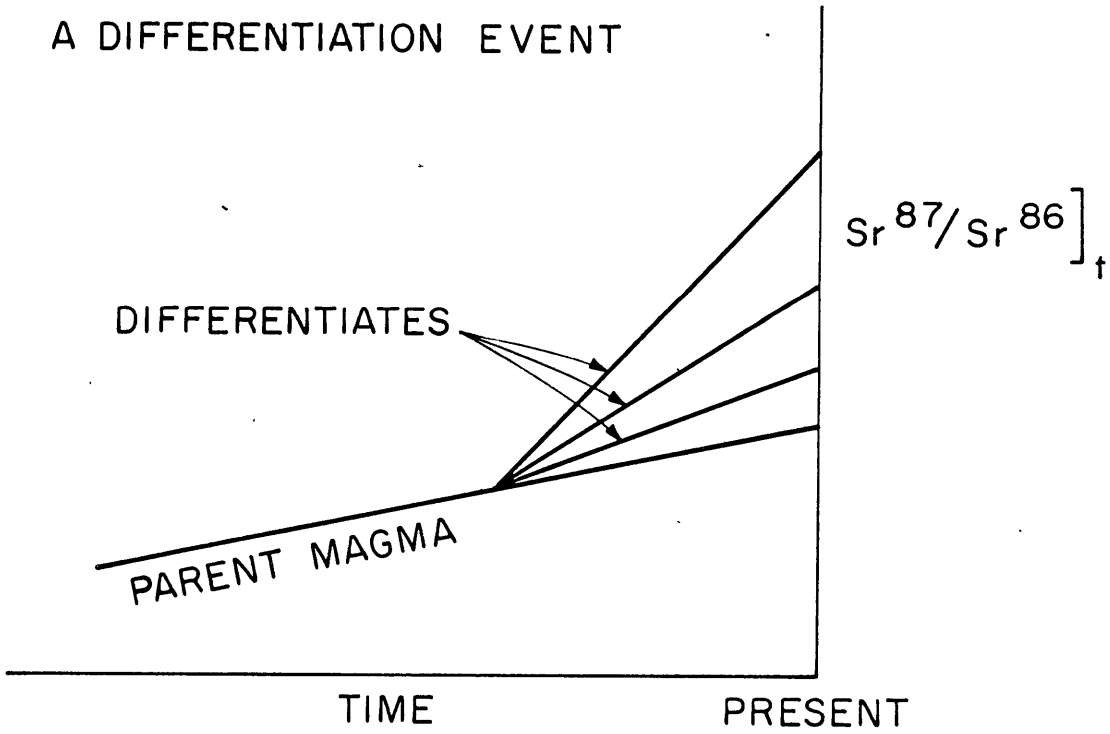
A. Sr^{87} Regression Diagram

B. A Differentiation Event

A. Sr^{87} REGRESSION DIAGRAM



B. A DIFFERENTIATION EVENT



series of comagmatic differentiates were formed from a parent magma. The Rb^{87}/Sr^{86} and Sr^{87}/Sr^{86} ratios for each differentiate are measured and plotted on the regression line diagram. Their point of intersection gives the age and strontium isotopic composition of the parent magma (Figure 1).

Regression line studies of recent basalts illustrate the last stage in Sr^{87}/Sr^{86} development of the magmas and, most important, their source regions in the upper mantle.

Initial Ratios. The initial ratio of Sr^{87}/Sr^{86} for any chemical system is the ratio that system had at the instant it became closed to the transfer of rubidium and strontium across its boundaries. In the case where the chemical system is composed of a number of subsystems, for example the mineral phases in an igneous rock, the initial ratio for each subsystem as well as the major system is the same.

Following the closure of the system, the Sr^{87}/Sr^{86} ratio increases with time at a rate that is proportional to the abundance of Rb^{87} in the system. In cases where the rubidium concentration is negligible compared with the strontium concentration, as in the case of carbonates, the growth of Sr^{87}/Sr^{86} with time is imperceptible. On the other hand, when the amount of rubidium is significant, the Sr^{87}/Sr^{86} ratio may increase measurably with time.

The initial Sr^{87}/Sr^{86} ratio for a system composed of a number of subsystems may be determined from the isochron diagram by projecting the isochron until it intersects the Sr^{87}/Sr^{86} axis. The point of intersection is $\left[Sr^{87}/Sr^{86}\right]_o$.

When there is only a single system present, the initial Sr^{87}/Sr^{86} ratio is found by correcting the observed ratio for the radiogenic strontium produced by Rb^{87} decay following closure of the system. This can be done only if the age of the system and the abundance of Rb^{87} is known. Recent basalts do not require a correction since there has not been a sufficient time lapse following closure of the system to produce a measurable increase in the radiogenic strontium. Therefore the observed ratio in these basalts is the initial ratio.

Samples

All the samples selected for analysis in this investigation are from the oceanic regions. No recent continental baslats are analyzed since it is felt that they may be significantly contaminated with crustal rubidium and strontium.

A total of 45 basalts are analyzed for their rubidium and strontium concentrations as well as for their Sr^{87}/Sr^{86} ratios. Eighteen of these are subalkaline dredge basalts having tholeiitic affinities. The remainder are from volcanic islands

in both the Pacific and Atlantic areas and have compositions varying from tholeiitic to trachytic. Figure 2 is a plot of % K_2O versus % SiO_2, similar to that of Engel, et al (1965), which shows the variable chemistry and the chemical groupings of all the basalts analyzed here.

The major element analyses and petrographic descriptions, where available, as well as the sample locations are described in detail in Appendix A.

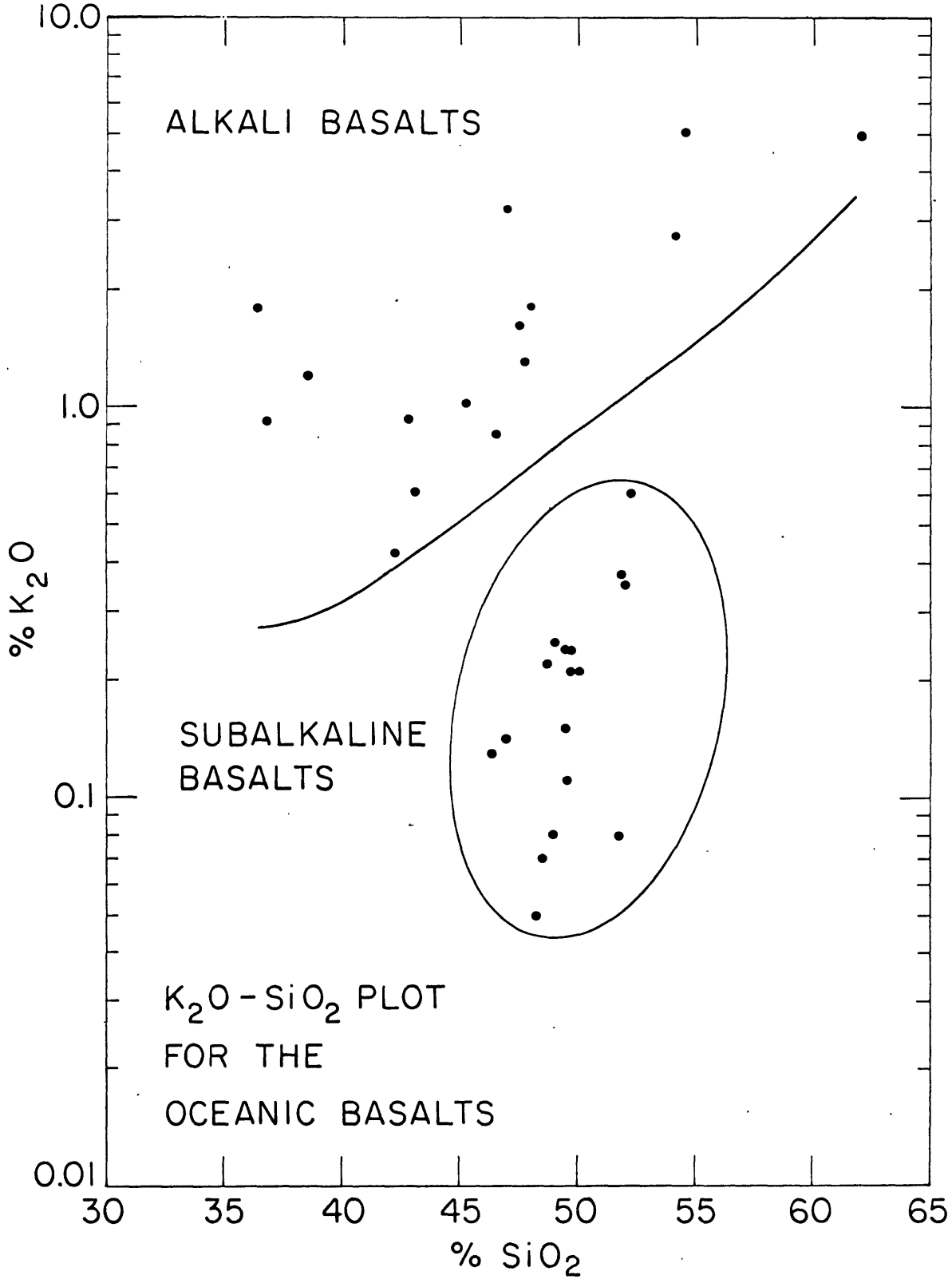
Eleven of the subalkaline basalts are from the mid-Atlantic Ridge. They were supplied by Vaughan Bowen of the Woods Hole Oceanographic Institution and A. E. J. Engel of the University of California. Engel also made the East Pacific Rise and Molokai fracture zone samples available for this study.

Seven samples of alkali basalts from the Canary Islands and Madeira were selected from a suite provided by N. Watkins of Florida State University. Unfortunately these samples have not yet been analyzed for major elements.

A trachyandesite and leucite trachy basalt from Tristan da Cunha were provided by J. D. H. Wiseman of the British Museum of Natural History. Tristan da Cunha is situated astride the mid-Atlantic Ridge in the south Atlantic.

FIGURE 2

K_2O-SiO_2 Relationships for the Oceanic Basalts


10.0
1.0
0.1
0.01
% K_2O
ALKALI BASALTS
SUBALKALINE
BASALTS
$K_2O - SiO_2$ PLOT
FOR THE
OCEANIC BASALTS
30
35
40
45
50
55
60
65
% SiO_2

J.G. Schilling, Massachusetts Institute of Technology provided an extensive suite of chemically analyzed basalts from the Hawaiian Islands. At the time this investigation was proceeding, the rare earth abundances were also being measured for these samples (Schilling and Winchester, 1966a,b,c). Included in this suite are tholeiitic basalts (including a diabase), nepheline basalts, a trachyte, and alkali-series basalts (including an alkaline-olivine basalt, ankaramite, mugearite, hawaiites, and basanite-basanitoid).

CHAPTER II

ANALYTICAL PROCEDURES

General Aspects

Rubidium and strontium concentrations are measured by isotope dilution techniques of mass spectrometry. The isotopic composition of strontium is determined both by isotope dilution measurements on spiked samples and by direct measurement on unspiked samples.

The procedures followed in preparing basalt samples for rubidium and strontium isotopic analysis are the standard methods adopted by the M.I.T. Geochronology Laboratory and are described in the Annual Progress Reports (Shields, 1964; Roe, 1964) and in the literature (Pinson, et al, 1965; Faure and Hurley, 1963). Samples with low concentrations of rubidium and strontium (< 10 micrograms/gram) require clean chemical treatment to ensure insignificant levels of rubidium and strontium contamination. In this investigation strontium contamination is not a determining factor since all the samples contain more than 100 micrograms/gram. The low concentrations of rubidium (.2 to 3 micrograms/gram) in oceanic tholeiites necessitate strict controls on both reagent and laboratory contamination levels at all stages of the investigation. To maintain these controls, blanks are prepared periodically along with and receive exactly the same treatment as the samples. In spite of the precautions

taken, minor discrepancies are found among replicate analyses of the same sample and may be attributed to any one or all of the factors:

1. Inhomogeneity of the sample, especially in the case of porphyritic basalts.
2. Discrepancies arising from chemical procedures. This includes contamination levels and erros in weighing and spiking.
3. Mass discrimination during spectrometer analysis. Unlike strontium, rubidium analyses cannot be normalized to correct for mass discrimination.

Sample Preparation

All of the samples prepared for chemical analysis in this investigation were small fragments (less than 50 grams) acquired from other laboratories. This is unfortunate because it is impossible to determine just how representative each fragment is of the total rock. It is most serious in the case of porphyritic basalts where the percentage of phenocrysts can be quite variable.

To remove surface oil films resulting from handling, each specimen is washed with demineralized water, and washed and dried with acetone. No acids are used in washing the specimens for fear of leaching out some of the strontium. Subsequent

handling is done with the aid of forceps. Initial crushing to about 50 mesh is by means of an acid-cleaned steel mortar and pestle followed by final grinding to about 150 mesh in a ball mill. Each piece of equipment is carefully washed with 2NHCl and demineralized water and dried with acetone before use. Samples are stored in tightly capped polyethylene bottles prior to analytical treatments.

In order that the correct amount of spike be added for the isotope dilution measurements, it is necessary to determine the approximate rubidium and strontium concentrations by x-ray fluorescence. The instrument used in the M.I.T. Geochronology Laboratory is a Norelco unit equipped with a molybdenum tube and topaz crystal. K_{α_1} peaks for Rb($2\theta = 39.9°$) and Sr($2\theta = 37.6°$) are scanned at a speed of 1° per minute and peak intensities are compared with those of the standard diabase W-1 (185 ppm Sr and 21 ppm Rb) run as an external standard before each unknown. The precisions for these fast-scan measurements are $\pm$ 8% for strontium and $\pm$ 15% for rubidium where concentrations are greater than ten micrograms per gram (Table 2). These are sufficiently accurate for spike calculations. The lower limit of detectability for rubidium is 5-10 ppm; consequently many of the samples, i.e. oceanic tholeiites, show no rubidium peak. For spiking purposes a concentration of 2-3 ppm is assumed.

Table 2

Accuracy of Fast-Scanning X-Ray Techniques for Determining Rubidium and Strontium for Spiking Purposes

Sample No.	X-Ray		Isotope Dilution		% Difference from I.D.	
	Rb ppm	Sr ppm	Rb ppm	Sr ppm	Rb	Sr
R5964	< 5	125	2.48	115		+8.7
R5965	< 5	138	2.61	133		+3.8
R5966	< 5	132	2.65	122		+8.2
R5967	< 5	130	2.89	127		+2.4
9948	8	317	2.18	329		-3.7
9960	19	1727	20.9	2150	-9.1	-19.5
9962	25	865	28.9	992	-13.5	-12.8
9982	19	553	22.9	635	-17	-12.9
1101	17	391	16.3	453	+4.3	-13.7
1102	35	1036	40.2	1107	-12.9	-6.4
1104	44	1079	58.4	1061	-24.6	+1.7
1106	22	815	28.3	908	-22.2	-10.3
10396	< 5	353	0.49	396		-10.9
10398	8	331	5.99	346	+33	-4.3
10403	10	407	6.43	432	+56	-5.8
				Average	|14.8|*	|8.3|%

Absolute % Difference

*Excluding samples with $\leq$ 10 ppm Rb.

Sample size for chemical treatment depends upon the concentrations of strontium and rubidium. For mass spectrometric analyses, 2-3 micrograms of strontium on the filament, if sufficiently free of impurities, provides a good run. Rubidium ionizes much more readily than strontium and samples less than one microgram provide adequate runs. As a general rule, sample sizes are chosen so that at least 100 micrograms of strontium is processed, leaving an adequate reserve in the event of a run failure.

Chemistry

Isotope Dilution Techniques. Isotope dilution analyses require addition of an exactly known amount of strontium "spike" to a precisely weighed sample. Spike solutions are prepared in 2000 ml lots, calibrated against standard shelf solutions by mass spectrometric techniques, and added by pipette to the samples under investigation (Shields, 1964; Roe, 1964). It is found by experience that the best precision is achieved if the Sr^{84}/Sr^{86} ratio of the spiked sample is unity and the sample is spiked accordingly.

The optimum Rb^{85}/Rb^{87} ratio for isotope dilution analyses is 0.5. The isotopic composition for natural rubidium is taken to be $Rb^{85}/Rb^{87} = 2.5995 \pm 0.0015$ (Shields, et al, 1963) while the spike employed in this investigation is $Rb^{85}/Rb^{87} = 0.0083$.

Spike solutions are added as the first step in the chemical process.

Preparation of Spike Solutions. Two Sr^{84}-enriched spikes were employed in the present investigation; an intermediate spike containing 4.85 micrograms Sr^{84}/ml (84-65/B and a dilute spike containing 1.036 micrograms Sr^{84}/ml (84-65/A). Both are prepared by dissolution in 2NHCl of Sr^{84}-enriched $Sr(NO_3)_2$ (batch number LH 1367 (A)) supplied by Oak Ridge National Laboratory. The concentrations of the two dilute spikes are determined by replicate analyses against three shelf solutions prepared in the M.I.T. laboratory and are reported in Table 3.

Two rubidium spike solutions are also used in this study. An intermediate spike contains 14.47 micrograms Rb/ml (87-65/B) and a dilute spike contains 2.89 micrograms Rb/ml (84-65/A). These spikes are also prepared by dissolution in 2NHCl of enriched $Rb^{87}Cl$ salts obtained from the Oak Ridge National Laboratory (batch number LY 1448(A)). The concentrations of these spike solutions are again obtained by calibration against standard shelf solutions. The results are reported in Table 4.

The procedures for calibrating the spike solutions are described in detail by Shields (1964).

Reagents. The reagents used in the digestion process are 2N vycor distilled HCl, vycor distilled HNO_3, 31N HF, and double vacuum distilled in vycor $HClO_4$. In spite of the care taken in preparing these reagents with a high degree of purity, they are still the most critical source for rubidium and strontium contamination and every effort is made to keep reagent volumes at a minimum.

Table 3

Summary of Spike Calibration Analyses Sr^{84} Spikes

Mass Spectrometer Record No.	Analyst	Sr μgm/ml	Sr^{84} μgm/ml	Remarks
Spike 84-65/A				
4220(S)*	RVS	1.291	1.042	Shelf RVS 65/1
4305(N)	RVS	1.279	1.032	Shelf RVS 65/2
4317(N)	RVS	1.289	1.040	Shelf RVS 65/1
Calculations from 65/B Calibrations				
		1.281	1.034	Shelf RVS 65/2
		1.286	1.038	Shelf RVS 65/1
		1.281	1.034	Shelf RVS 65/1
		1.279	1.032	Shelf RVS 65/1
		1.284 ± .005	1.036 ± .004	
Spike 84-65/B				
4294(L)	RVS,HWF	6.005	4.846	Shelf RVS 65/2
4421(N)	RVS	6.032	4.868	Shelf RVS 65/2
4359(S)	AEB	6.005	4.846	Shelf RVS 65/1
4364(S)	AEB	5.997	4.837	Shelf RVS 65/1
4661(I)	AEB,SAH	6.030	4.866	Shields' Shelf
		6.014 ± .017	4.852 ± .014	

*Letter in parentheses refers to mass spectrometer used.

Table 4

Summary of Spike Calibration Runs on Dilute and Intermediate Rb^{87} Spikes

Mass Spectrometer Number	Analyst	Rb^{87} µgm./ml	Rb µgm/ml	Remarks
Spike 87-65/A				
4357(S)*	AEB	2.86	2.88	M.I.T. Shelf
Calculations from 87-65/B		2.87	2.89	Shields' Shelf
		2.91	2.93	Shields' Shelf
		2.84	2.86	M.I.T. Shelf
		2.87	2.89	M.I.T. Shelf
		2.88	2.90	RVS - 65/1
		2.86	2.88	RVS - 65/1
		2.87 ± .022	2.89 ± .022	
Spike 87-65/B				
4315(L)	RVS	14.35	14.47	Shields' Shelf
4327(L)		14.53	14.65	Shields' Shelf
4313(L)		14.21	14.33	M.I.T. Shelf
4307(L)		14.33	14.45	M.I.T. Shelf
4325(L)		14.39	14.51	RVS - 65/1
4323(L)		14.31	14.43	RVS - 65/1
		14.35 ± .10	14.47 ± .10	

*Letter in parentheses refers to mass spectrometer used.

2N HCl is prepared in the laboratory by vycor distillation of reagent grade 6N HCl. Acid prepared in this manner has an extemely low level of strontium contaminants--about 4×10^{-5} micrograms/gram (Pinson, et al, 1965). Nitric acid is prepared in a similar manner but only a few mls are used for each sample so that the contribution to the level of contaminants is negligible.

Seventy percent perchloric acid, double vacuum distilled in vycor and shipped in vycor ampules (two lb. lots) was obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio. Similarly prepared H_2SO_4 may be obtained from the same company.

Pinson, et al (1965) noted that commercially prepared, analytical reagent grade, hydrofluoric acid contained significant amounts of strontium contaminants. Since that time, the M.I.T. laboratory has prepared hydrofluoric acid by bubbling HF gas through demineralized water using teflon equipment. A detailed description of the equipment and the procedures for preparing this acid is reported by Shields (1964). Blank analyses prepared in this study first using commercial HF and then the special HF indicate that the strontium contamination is halved by using the latter.

It should be noted that since the work of Wasserburg, Wen, and Aronson (1964) conclusively demonstrated pyrex glassware to be a major source of strontium contamination, this laboratory has replaced all glassware, used for acid solutions, with vycor or polypropylene. Vycor stills are used in preparing all reagents,

vycor ion exchange columns are employed for rubidium-strontium separation, and 5 ml vycor beakers for sample ignition and storage. Ion exchange fractions are collected in 100 ml polypropylene beakers.

Digestion Procedures. Both spiked and unspiked samples are dissolved in platinum dishes using 15 mls HF and 2 mls $HClO_4$ per gram of sample and taken to dryness. The solid residue is taken up in 100 mls of 2NHCl, evaporated to dryness, and taken up in another 50 mls 2NHCl, evaporated to 10-15 mls, and diluted to 40-50 mls with demineralized water. Solid residues remaining at this stage are removed by filtering and the filtrate stored in polypropylene beakers ready for ion exchange separation.

Ion Exchange. Separation of rubidium and strontium is accomplished on vycor ion exchange columns using Dowex 50-8x, 200-400 mesh, cation exchange resin, supported on a quartz-fiber mat. Each sample is washed through a 25 cm x 2.5 cm column of resin with approximately 800 mls of vycor distilled 2NHCl. The order for cation elution from this column is Na, K, Rb, Ca, Sr from first removed to last. Since there is considerable overlap of the cations, the eluant is collected in small volumes (less than 40 mls). Strontium collection is monitored by a carrier-free Sr^{85} tracer added to each sample prior

to placement on the column. Unfortunately a comparable rubidium tracer can no longer be obtained commercially so rapid analyses for rubidium are made by means of a Perkin-Elmer atomic absorption spectrophotometer.

Sample Ignition. The selected sample fractions are evaporated to dryness, transferred to 5 ml vycor beakers containing several drops of $HCLO_4$ to oxidize organic resin material, and then taken to dryness. Ignition over a Bunsen flame eliminates perchlorates. Strontium is converted to $Sr(NO_3)_2$ by the addition of one or two mls of HNO_3 and evaporation to dryness. The sample is now ready for mass spectrometer analysis.

Rubidium samples are treated in a slightly different manner to remove alumina which passes through the column with rubidium and is present as a white precipitate following ignition. After ignition, 3 mls of demineralized water is added to each sample while stirring and heating over a hot plate. Rubidium and potassium are soluble in hot water whereas the alumina is relatively insoluble and an effective separation is made by centrifuging. In this manner, about 3/4 of the alumina is removed. Rubidium is converted to nitrates in the same manner as strontium.

Laboratory Contamination

In spite of the precautions taken to ensure a minimum of contamination during the chemical procedure, there is a

measurable level of strontium and rubidium contamination primarily due to laboratory fallout. Blanks are run periodically along with the samples to keep a close check on these contamination levels and to apply corrections to the rubidium and strontium measurements. All reagents, including spikes, are added to empty platinum dishes in exactly the same volumes as those added to the samples. The blanks are carried through ion-exchange separation and ignition so that contamination levels are reported for procedures rather than reagents. Table 5 lists the results of blank analyses carried out through the period of this investigation.

Table 5

Contamination Levels for Rubidium and Strontium

Rb μgm/gm	Sr μgm/gm	Comments
.095	.024	Special HF
.065	.015	"
.025	———	"
.008	———	"
———	———	
Avg..048 ± .020 μgm/gm	.020 ± .005 μgm/gm	
.046	.034	Commercial HF

the blanks contain approximately double the rubidium contamination reported by Pinson, et al (1965) and Shields (1964). Two explanations are offered for this higher level.

1. The water used in chemical processing was purified only to the extent of demineralization. It was not vycor distilled.
2. During the period that elapsed between this investigation and those by Pinson and Shields, the M.I.T. Geochronology Laboratory was moved to new quarters in the Cecil Green Earth Sciences Building. Laboratory fallout contamination may be higher in the new location.

Mass Spectrometry

Description. Three mass spectrometers were used in the course of this investigation. The strontium and the majority of the rubidium isotope dilution measurements were made on a 60° sector, six inch radius, single filament, solid source, single collector Nier-type instrument (Sally*). The ion beam is amplified by a Carey Model 31 vibrating reed electrometer and the output is recorded on a Brown strip-chart recorder. The mass range is scanned mechanically by a reversing magnet sweep. For strontium analyses, the required vacuum (approximately 5×10^{-7} mm Hg

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*For purposes of identification, each of the five mass spectrometers in the M.I.T. Geochronology Laboratory is assigned a name.

measured by a Veeco ion gauge located near the source) is obtained by a combination of a Duo-seal forepump, mercury diffusion pump, and liquid nitrogen cold trap.

Subalkaline oceanic basalts rubidiums were analyzed on a Nuclide Corporation six-inch mass spectrometer (Nancy), modified to permit peak-hopping. This was invaluable for analyzing samples with very low rubidium concentrations since statistically meaningful data could be obtained in a short period of time.

Strontium isotope ratios of the Canary Island suite and four dredge samples from the East Pacific Rise were measured by P. M. Hurley on a 12-inch, 60° sector, triple filament instrument (Connie). This machine is built by Consolidated Electrodynamics Corporation. It is equipped with an expanded scale recorder which gives a higher degree of precision than that obtained for the six-inch machines.

Technique. A tantalum filament .002" x .001" is spot welded to two filament posts in the mass spectrometer source. This filament is cleaned in the mass spectrometer by baking for 15 minutes at 2.5 amps to remove any rubidium contamination. The absence of this contamination is confirmed by scanning the mass 85 position at the high current.

The samples, now in the form of strontium nitrate are dissolved in a single drop of vycor distilled nitric acid and loaded on the filament by means of a vycor capillary syringe

which is stored in a nitric acid bath when not in use. A current of about 1 amp is passed through the filament evaporating the acid and leaving the sample as a thin film of strontium or, as the case may be, rubidium nitrate. Prior to running, samples are conditioned in the mass spectrometer for 8 hours at pressures lower than 7×10^{-6} mm Hg and currents of 1.1 and 0.5 amps for strontium and rubidium respectively.

Strontium analyses are conducted on 2-3 micrograms of sample at 1.7 - 2.0 amps and pressures of 5×10^{-7} mm Hg. Pressures higher than 1×10^{-6} result in poor peak resolution. For best precision Sr^{86} peak heights of 7-9 inches are maintained when possible. The mass range 84-88 is scanned for isotope dilution measurements and 86-88 for isotope ratios. Preceeding each run, the position for mass 85 is scanned at a more sensitive scale than that used in the standard run to make certain that there is no rubidium contribution to the 87 peak.

At least sixty complete scans with continuing steady emission is considered to give sufficiently representative data. Peak heights are summed and ratios obtained for every six scans. The final ratios are averages of the sets of six.

Rubidium samples of approximately one microgram are run with a filament current .6 - .9 amps and pressures less than 1×10^{-5} mm of Hg. The mass range 85 to 87 is scanned about 30 times using the peak-hopping technique.

Analytical Precision

Replicate Analyses of Eimer and Amend Strontium Carbonate Standard. Over a period of months, mass spectrometer characteristics may change significantly. For this reason, a standard strontium carbonate is run periodically (in practice, once every two weeks). By running this same standard on different instruments, it is possible to make a comparison of data. More important, interlaboratory comparison of Sr^{87}/Sr^{86} ratios can be made. Unfortunately the importance of analyzing this standard has not yet been recognized by some laboratories and the data they report cannot be compared with that reported by laboratories who make it a practice to analyze the standard periodically. During the course of this investigation, a number of samples were analyzed in duplicate on different instruments and the data compared by using the results of the standard carbonate analyses. Standard carbonate analyses for "Sally" are reported in Table 6 and those for "Connie" in Table 7. The error in a single measurement, given as the standard deviation, is calculated from the formula:

$$\sigma = \pm \sqrt{\frac{\sum_{i=1}^{n} |x_i - \bar{x}|^2}{n - 1}}$$

where x_i is the value for the "i" th analysis, $\bar{x}$ is the average of all the analyses, and n is the number of analyses. The

Table 6

Analyses of Eimer and Amend Strontium Carbonate Standard

Throughout the Period of This Investigation

Record No.	Date	No. Scans	86/88	87/86*	Analyst
4187(S)	4/14/65	72	.1189	.7079	RVS
4227(S)	7/20/65		.1186	.7084	MH
4262(S)	11/2/65	60	.1184	.7081	AEB
4264(S)	11/3/65	60	.1181	.7083	AEB
4265(S)	11/4/65	42	.1182	.7082	AEB
4367(S)	1/18/66	42	.1174	.7080	HWF
4520(S)	3/28/66	60	.1187	.7076	AEB
4557(S)	4/9/66	42	.1180	.7080	AEB
4624(S)	5/2/66	60	.1187	.7075	AEB
4662(S)	5/15/66	48	.1191	.7084	AEB
4669(S)	5/17/66	48	.1191	.7085	AEB
4728(S)	6/10,11/66	18	.1193	.7082	AEB,DGB
4762(S)	6/23,24/66	36	.1184	.7082	DGB

Average 86/88 $.1185 \pm .0005$ $2\sigma = .001$

87/86* $.7081 \pm .0003$ $2\sigma = .0006$

(S) mass spectrometer "Sally"

* normalized to $Sr^{86}/Sr^{88} = .1194$

RVS R. Van Schmus

MH M. Heath

HWF H. W. Fairbairn

AEB A. E. Bence

DGB D. G. Brookins

Table 7

Replicate Analyses of Eimer and Amend Strontium Carbonate Standard on Connie Throughout the Period of This Investigation

86/88	87/86*	Analyst
.1192	.7071	P. M. Hurley
.1192	.7076	"
.1193	.7079	"
.1192	.7081	"
.1190	.7077	"
.1190	.7076	"
.1192 ± .0001	.7077 ± .0003	
2σ = ± .0003	2σ = ± .0006	

*Normalized to Sr^{86}/Sr^{88} = .1194

confidence limit of σ is 66 2/3% whereas the 95% confidence level is 2σ.

Replicate Analyses of Selected Samples. Replicate analyses on separate weighings of selected individual samples are conducted as further evidence for the authenticity of the measurements. The results of these analyses are reported in Tables 8 and 9. Standard deviations for the duplicate pairs are determined from the following equation from Youden (1951)

$$S.D. = \pm \sqrt{\frac{\sum_{i=1}^{n} \left| x_i^1 - x_i^2 \right|^2}{2n}}$$

where x_i^1 and x_i^2 are the duplicate analyses of the "i"th sample and n is the number of samples.

Determination of "Calculated" Strontium Isotopic Composition

General. Sr^{87}/Sr^{86} ratios may be computed from isotope dilution analyses if the spike is sufficiently enriched in Sr^{84}. A highly enriched Sr^{84} spike permits corrections for discrimination or fractionation effects in the mass spectrometer and calculation of the Sr^{87}/Sr^{86} ratios and concentrations of total strontium from the same data, thus conserving time and sample.

Table 8

Reproducibility of Strontium Analyses

Sample No.	Sr^{87}/Sr^{86N} Calculated	Diff x_1-x_2	Diff^2 $(x_1-x_2)^2$	Sr Conc.	Diff	Diff^2
JP 16	.7029			1759		
	.7024	.0005	.00000025	1746	13	169
9960	.7043			2155		
	.7043	.0000	.00000000	2145	10	100
R5950	.7018			113.4		
	.7039	.0021	.00000441	114.3	.9	.81
R5974	.7033			135.97		
	.7048	.0015	.00000225	135.70	.27	.073
			.00000791			269.883

$$S.D. = \sqrt{\frac{.00000791}{8}} = \pm .0010$$

$$S.D. = \sqrt{\frac{269.883}{8}} = \pm 6.7$$

Table 9

Reproducibility of Rubidium Analyses

Sample No.	Rb µgm/gm	Diff x_1-x_2	Diff^2 $x_1-x_2^2$
JP16	46.5		
	46.7		
	46.6	.2	.0400
R5964	2.50		
	2.46		
	2.48	.04	.0016
R5965	2.61		
	2.61		
	2.61	.00	.0000
R5966	2.65		
	2.62		
	2.67		
	2.65	.05	.0025
R5967	2.87		
	2.90		
	2.89	.03	.0009
10396	0.50		
	0.50		
	0.46		
	0.49	.04	.0016

$$S.D. = \pm \sqrt{\frac{.0466}{12}} = \pm 0.062$$

If spiking is carried out so that the Sr^{84}/Sr^{86} ratio in the mixture is between 0.5 and 1.5, the following computations may be made. This method of determining the Sr^{87}/Sr^{86} ratios from the isotope dilution data, recently introduced to the M.I.T. Geochronology Laboratory, is standard procedure at other laboratories. I am indebted to W. R. Van Schmus who instructed me in the development and use of these computations.

Normalization Procedures. The atomic ratios of Sr^{84}, Sr^{86}, Sr^{87}, and Sr^{88} relative to Sr^{86} are determined for the sample plus spike mixture from the mass spectrometer data. The following notations are used to designate these ratios:

$$Sr^{84m}/Sr^{86m},\ Sr^{86m}/Sr^{86m},\ Sr^{87m}/Sr^{86m},\ \text{and}\ Sr^{88m}/Sr^{86m}$$

where "m" is the mixture of sample plus spike. In the following equations, the notations "s" and "t" are sample and spike or tracer strontium respectively. For any isotope A of strontium,

$$Sr^{As} = Sr^{Am} - Sr^{At} \qquad (1)$$

The following molar ratios now may be written

$$NSr^{86s}/NSr^{84t} = \frac{Sr^{86m}/Sr^{84m} - Sr^{86t}/Sr^{84t}}{1 - (Sr^{84s}/Sr^{88s})(Sr^{88m}/Sr^{84m})} \qquad (2)$$

and

$$NSr^{88s}/NSr^{84t} = \frac{Sr^{88m}/Sr^{84m} - Sr^{88t}/Sr^{84t}}{1 - (Sr^{84s}/Sr^{88s})(Sr^{88m}/Sr^{84m})} \qquad (3)$$

where N means a molar quantity. Dividing (1) by (2) gives

$$Sr^{86s}/Sr^{88s} = \frac{[Sr^{86m}/Sr^{84m} - Sr^{86t}/Sr^{84t}][1-(Sr^{84s}/Sr^{88s})(Sr^{88m}/Sr^{84m})]}{[Sr^{88m}/Sr^{84m} - Sr^{88t}/Sr^{84t}][1-(Sr^{84s}/Sr^{86s})(Sr^{86m}/Sr^{84m})]} \qquad (4)$$

The accepted Sr^{86s}/Sr^{88s} ratio is 0.1194 but is rarely obtained due to mass spectrometer fractionation or discrimination of the isotopes. Consequently, it is necessary to "normalize" the original atomic ratios to give a calculated Sr^{86s}/Sr^{88s} ratio of 0.1194. The correction factors applied are

$$\frac{Sr^{86s}/Sr^{88s}}{.1194} \qquad (5)$$

for a two mass unit correction and

$$\frac{Sr^{86s}/Sr^{88s} + .1194 - \frac{Sr^{86s}/Sr^{88s}}{2}}{.1194} \qquad (6)$$

for a one mass unit correction.

The corrected ratios are

Table 10

Isotopic Composition of Strontium

Natural Strontium

86/88 = .1194

84/88 = .0068

Spike Strontium

Run	86/84	87/84	88/84	Analyst
4191(S)[1]	0.0468	0.0158	0.1387	RVS
4272(L)[1]	0.0474	0.0159	0.1378	HWF
ORNL	0.0469	0.0156	0.1381	ORNL
Average	0.0469 ± 0.0004	0.0158 ± 0.0002	0.1382 ± 0.0005	

[1]Data from Mass Spectrometer Sally (S) and Lulu (L).

$$\frac{Sr^{84m}/Sr^{86m}}{(5)} = Sr^{84m}/Sr^{86m}\ (\text{corrected}) \qquad (7)$$

$$Sr^{87m}/Sr^{86m} \times (6) = Sr^{87m}/Sr^{86m}(\text{corrected}) \qquad (8)$$

$$Sr^{88m}/Sr^{86m} \times (5) = Sr^{88m}/Sr^{86m}(\text{corrected}) \qquad (9)$$

The procedure is repeated as many times as is necessary until $Sr^{86s}/Sr^{88s} = 0.1194$.

The isotopic compositions of natural strontium and of the Sr^{84}-enriched spike used in this study are given in Table 10.

Calculation of Sr^{87}/Sr^{86} Isotopic Ratios. The calculation of the Sr^{87s}/Sr^{86s} ratio requires more elaborate computations since the value of radiogenic Sr^{87} increases with time. An equation similar to (2) and (3) may be written for the molar Sr^{87s}/Sr^{84s} ratio using the normalized ratios

$$NSr^{87s}/NSr^{84t} = \frac{Sr^{87m}/Sr^{84m} - Sr^{87t}/Sr^{84t}}{1-(Sr^{84s}/Sr^{87s})(Sr^{87m}/Sr^{84m})} \qquad (10)$$

But

$$Sr^{84s}/Sr^{87s} = \frac{[Sr^{86m}/Sr^{84m} - Sr^{86t}/Sr^{84t}]}{[Sr^{86s}/Sr^{84s} - Sr^{86m}/Sr^{84m}]} \cdot \frac{NSr^{84t}}{NSr^{87s}} \qquad (11)$$

substituting in (10) and combining with (2) gives

$$Sr^{87s}/Sr^{86s} = [1-(Sr^{84s}/Sr^{86s})(Sr^{86m}/Sr^{84m})] \times \left[\frac{Sr^{87m}/Sr^{84m} - Sr^{87t}/Sr^{84t}}{Sr^{86m}/Sr^{84m} - Sr^{86t}/Sr^{84t}} + \frac{Sr^{87m}/Sr^{84m}}{Sr^{86s}/Sr^{84s} - Sr^{86m}/Sr^{84m}}\right] \quad (12)$$

the normalized Sr^{87}/Sr^{86} ratio.

Calculation of Rubidium and Strontium Concentrations from Isotope Dilution Measurements

Strontium. Total strontium concentrations are calculated in each sample by determining the concentration and weight percent of Sr^{86} as follows.

$$\text{Weight \% } Sr^{86} = \frac{Sr^{86}/Sr^{88}(wt)}{\sum \frac{Sr^{84} + Sr^{86} + Sr^{87} + Sr^{88}}{Sr^{88}}(wt)}$$

where

$$Sr^{84}/Sr^{88} = .0068 \times 83.94$$
$$Sr^{86}/Sr^{88} = .1194 \times 85.94$$
$$Sr^{87}/Sr^{88} = Sr^{87}/Sr^{86} \times .1194 \times 86.94$$
$$Sr^{88}/Sr^{88} = 1.0000 \times 87.94$$

$$Sr^{86}_{ppm} = NSr^{86s}/NSr^{84t} \times 86/84 \text{ Atomic Ratio} \times \frac{\text{Volume spike} \times \text{con. } Sr^{84}/\text{ml spike}}{\text{Sample weight}}$$

where NSr^{86s}/NSr^{84t} is the molar ratio obtained in the previous section.

$$\text{Then total Sr} = \frac{Sr^{86}\ \mu gm/gm}{\text{wt \% } Sr^{86}} .$$

Rubidium. Rubidium concentrations are calculated from the Rb^{85}/Rb^{87} ratio obtained for the spike sample given the 85/87 ratios for both natural rubidium and the spike employed. The isotopic compositions of natural rubidium and the rubidium spike employed in this study are given in Table 11. The calculations are as follows:

$$\frac{85m}{87m} = \frac{85n}{87n} + \frac{85s}{87s}$$

where subscripts m, n and s refer to mixture, normal and spike rubidium respectively.

Substituting,

$$\frac{85m}{87m} = \frac{.7215n + .0082s}{.2785n + .9918s}$$

$85/87\Big|^{m}$ is determined from the spectrometer run.

Table 11

Rubidium Computations

Normal Rubidium

Atom fractions	Weight fractions
Rb^{85} = 0.7215	0.7168
Rb^{87} = 0.2785	0.2832
1.0000	1.0000

Spike Rubidium

Atom fractions	Weight fractions
Rb^{85} = 0.0082	0.0080
Rb^{87} = 0.9918	0.9920
1.0000	1.0000

Weight Factor Calculations

Natural Rb	Spike Rb
85 x .7215 = 61.33	85 x .0082 = 0.70
87 x .2785 = 24.23	87 x .9918 = 86.29
85.56	86.99

$$\frac{\text{Normal}}{\text{Spike}} \text{ (Weight Factor)} = \frac{85.56}{86.99} = .9836$$

Then solve for n/s ratio and

Total Rb = n/s ratio x wt. factor x

$$\frac{\text{Vol. Rb spike x conc. Rb spike } \mu\text{gm/ml}}{\text{Sample weight}} .$$

No correction for mass discrimination is possible for rubidium computations.

Comparison of Calculated Sr^{87}/Sr^{86} with Measured Sr^{87}/Sr^{86} Ratios

Calculated Sr^{87}/Sr^{86} ratios are determined from the isotope dilution analyses by the method described above. Measured Sr^{87}/Sr^{86} ratios are obtained directly from the analyses of unspiked samples and are believed to closely approximate the true isotopic ratio. Selected suites of samples are analyzed by both isotope dilution and isotope ratio techniques to compare the two methods. These data are reported in Table 12. The measured Sr^{87}/Sr^{86} were analyzed on the 12-inch machine (Connie) which gave a standard carbonate Sr^{87}/Sr^{86} ratio of .7077. The data are corrected to a Sr^{84}/Sr^{86} ratio of .7081 to bring them in line with the data from the 6-inch machine (Sally).

There does not appear to be any consistent significant differences between the calculated and measured isotope ratios.

Table 12 Comparisons of Calculated and Measured Sr^{87}/Sr^{86} Ratios

Sample No.	$Sr^{87}/Sr^{86}\|^{N}_{\text{calculated}}$ (x_1)	$Sr^{87}/Sr^{86}\|^{N^1}_{\text{measured}}$	$Sr^{87}/Sr^{86}\|^{N^2}_{\text{measured}}$ (x_2)	x_1-x_2	$\|x_1-x_2\|^2$
R5810	.7033	.7024	.7036(S)		
			.7028		
			Avg. .7032	+.0001	.00000001
R5811	.7035	.7032	.7036	-.0001	.00000001
R5814	.7033	.7030	.7034	-.0001	.00000001
R5816	.7039	.7033	.7037	+.0002	.00000004
R5817	.7034	.7035	.7039	-.0005	.00000025
R5832	.7030	.7031	.7035	-.0005	.00000025
R5964	.7034	.7030	.7034	.0000	.00000000
R5966	.7039	.7028	.7031(S)		
			.7032		
			Avg. .7032	+.0007	.00000049
					Σ.00000106

$$\sigma = \pm \sqrt{\frac{.00000106}{16}} = \pm .0002^{6} = \pm .0003$$

N Normalized to $Sr^{86}/Sr^{88} = .1194$

1 Data from Connie; E and A standard carbonate $Sr^{87}/Sr^{86} = .7077$

2 Connie data corrected to standard $Sr^{87}/Sr^{86} = .7081$

(S)Isotope Ratio analyzed on Sally.

CHAPTER III

RESULTS

Atlantic Ocean

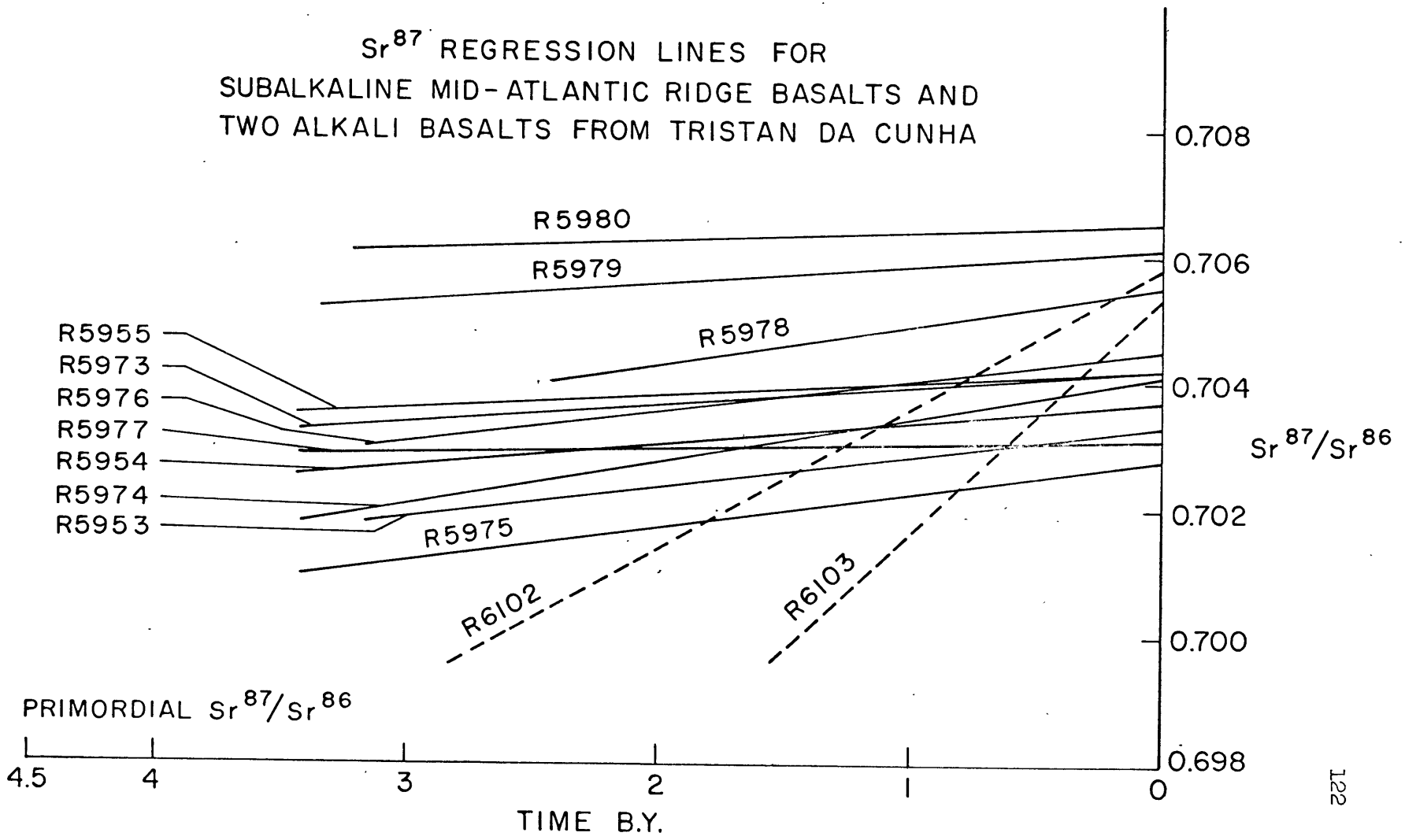
Mid-Atlantic Ridge Dredge Basalts. The results of rubidium and strontium analyses for eleven mid-Atlantic Ridge dredge basalts having tholeiitic affinities are given in Tables 13 and 14. With only a few exceptions the Sr^{87}/Sr^{86} ratios are in the range .7028 to .7042 with the average .7037. The average Rb/Sr ratio is .0073 and from Figure 3 it is seen that the Sr^{87} regression lines projected back to 4.5 billion years fall considerably above the assumed primordial Sr^{87}/Sr^{86} ratio for the earth.

The average abundances of rubidium and strontium (0.98 ppm and 138.7 ppm respectively) are low compared to the majority of basaltic rocks. The combination of low rubidium and strontium concentrations, low Rb/Sr ratios, and the observed Sr^{87}/Sr^{86} ratios suggest that the upper mantle source region for these basalts was depleted in trace elements prior to the generation of the subalkaline magmas. The generation of much of the radiogenic strontium in those basalts must have occurred prior to the removal of the trace elements.

The potassium concentrations are calculated from the chemical analyses of these dredge basalts (Appendix A) and K/Rb

FIGURE 3

Sr^{87} Regression Lines for Subalkaline Mid-Atlantic Ridge Basalts and Two Alkali Basalts from Tristan da Cunha


Sr87 REGRESSION LINES FOR
SUBALKALINE MID-ATLANTIC RIDGE BASALTS AND
TWO ALKALI BASALTS FROM TRISTAN DA CUNHA
R5980
R5979
R5978
R5955
R5973
R5976
R5977
R5954
R5974
R5953
R5975
R6102
R6103
0.708
0.706
0.704
0.702
0.700
0.698
Sr87/Sr86
PRIMORDIAL Sr87/Sr86
4.5
4
3
2
1
0
TIME B.Y.

ratios are determined (Table 14). These ratios are the highest observed for terrestrial material but fall over quite a wide range.

Canary Islands and Madeira. Analyses of the subalkaline oceanic basalts and alkaline volcanics, that cap the islands in the ocean basins, point towards an upper mantle that has, on a regional scale, minor heterogenities with respect to Rb/Sr ratios, yet is locally very homogeneous. Seven alkaline basalts from the Canary Islands and Madeira, selected on the basis of variability of Rb/Sr ratios, have remarkably consistent Sr^{87}/Sr^{86} ratios (.7032 to .7039 averaging .7035) (Table 15). The abundances of strontium and rubidium vary from about 650 to 1200 and 20 to 80 respectively. With one exception, the Rb/Sr ratios are from .025 to .035 (Table 15). Both strontium and rubidium are enriched in these basalts when compared with the subalkaline basalts of the mid-Atlantic Ridge. Rubidium, however, is enriched to a greater degree than strontium.

The Sr^{87} regression lines for these samples (Figure 4) fan out on both sides of the primordial Sr^{87}/Sr^{86} ratio at 4.5 billion years.

It is important to note that the average Sr^{87}/Sr^{86} ratio for the Canary basalts is similar to the average obtained for the subalkaline oceanic basalts.

FIGURE 4

Sr^{87} Regression Lines for Canary Islands and Madeira

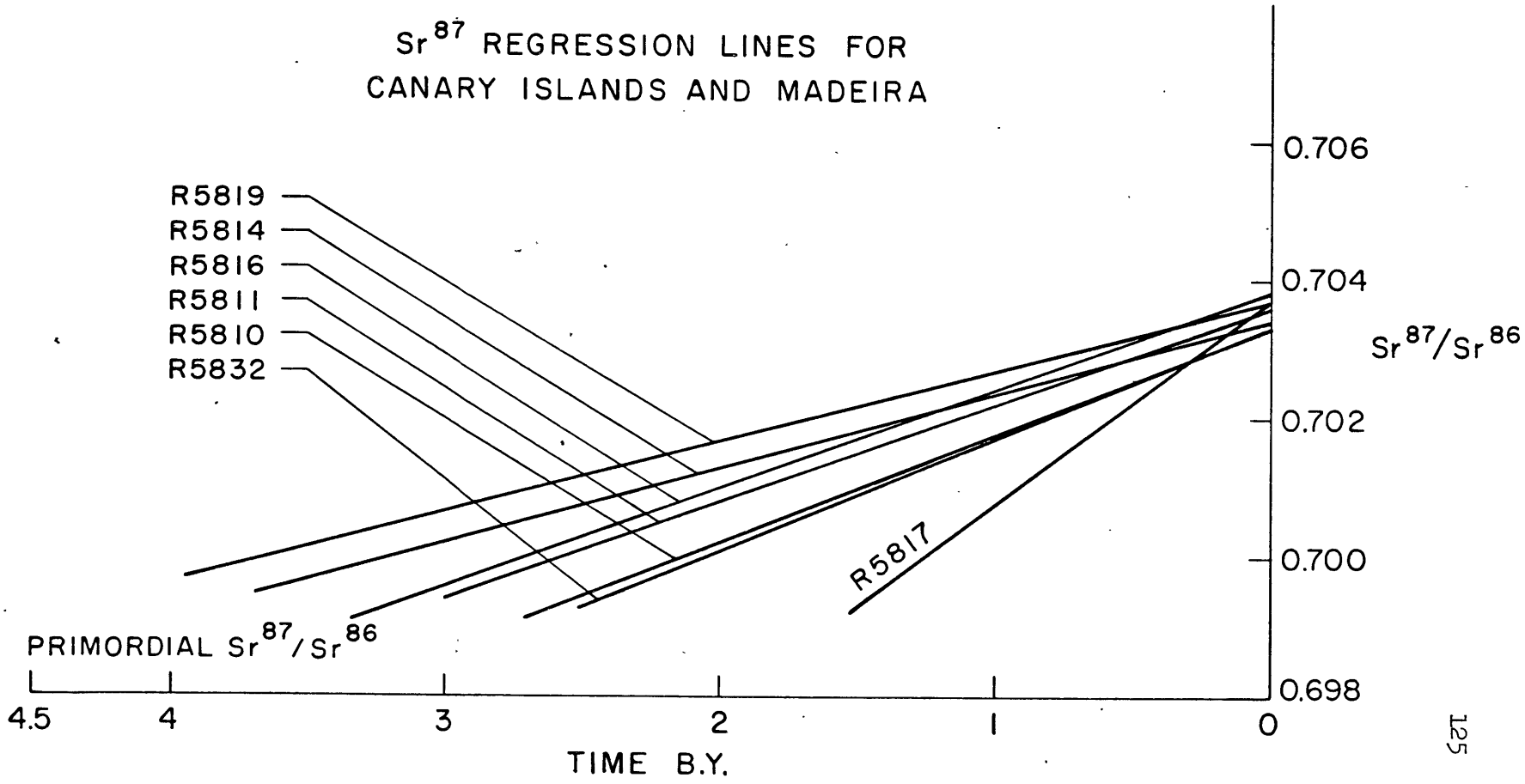

Sr87 REGRESSION LINES FOR
CANARY ISLANDS AND MADEIRA
R5819
R5814
R5816
R5811
R5810
R5832
R5817
0.706
0.704
0.702
0.700
0.698
Sr87/Sr86
PRIMORDIAL Sr87/Sr86
4.5
4
3
2
1
0
TIME B.Y.

Table 13

Mid-Atlantic Ridge Dredge Basalts

Sample No.	Location	$Sr^{87}/Sr^{86}\big\|^{N}_{C}$	Rock Type
R5953	5°47'S 11°25'W	.7033(1)[2]	
R5954	9°39'N 40°27'W	.7037(1)	
R5955	9°39'N 40°27'W	.7042(1)	
R5973	about 22°N	.7042(1)	Greenstone
R5974	about 22°N	.7041(2)	Fresh basalt
R5975	about 22°N	.7028(1)	Greenstone
R5976	about 22°N	.7045(1)	Greenstone
R5977	about 22°N	.7031(1)	Greenstone
	Average	.7037	
R5978	22°56'N 46°35'W	.7055(1)[1]	Basalt
R5979	22°56'N 46°35'W	.7061(1)[1]	Basalt
R5980	22°56'N 46°35'W	.7065(1)[1]	Basalt

N Normalized to 86/88 = .1194

C Calculated

1 These samples were taken from different portions (see text) of the basalt boulder described by Ciffelli, (1965) and Nicholls, et al, (1964).

2 Figures in parentheses indicate number of analyses.

Table 14

Mid-Atlantic Ridge Dredge Samples

Sample No.	K_2O%	Kppm	Rbppm[1]	Srppm	Rb/Sr	K/Rb
R5953	.24	1990	1.47	135.7	.0108	1355
R5954	.08	664	1.19	155.7	.0077	558
R5955	.21	1740	0.51	121.9	.0042	3415
R5973	.14	1160	0.66	101.2	.0065	1760
R5974	.25	2075	2.10	135.8	.0155	1010
R5975	.21	1740	1.57	137.2	.0114	1110
R5976	.08	664	0.21	184.1	.0011	3160
R5977	.05	415	0.15	138.2	.0011	2765
		Avg.	0.98	138.7	.0073	
Basalt Boulder						
R5978			2.52	193.7	.0132	
R5979			1.52	238.0	.0064	
R5980	.13	1080	1.28	348.0	.0037	847

[1]Corrected for Rb blank .048ppm

Table 15

Atlantic Ocean Islands

Tristan da Cunha

Sample No.	Name	Sr^{87}/Sr^{86} N	Kppm	Rbppm	Srppm	Rb/Sr	K/Rb
R6102	Leucite trachybasalt	.7058	2820	90	1806	.050	313
R6103	Trachyandesite	.7053	4175	121	1481	.082	345
	Average	.7055					

Canary Islands and Madeira

Sample No.	Island	Sr^{87}/Sr^{86} N	Rbppm	Srppm	Rb/Sr
R5810	Hierro	.7032*	36.1	1078	.034
R5811	Hierro	.7036*	25.5	812	.031
R5814	Gomera	.7034*	17.4	739	.024
R5816	Gomera	.7037*	21.2	682	.031
R5817	Teneriffe	.7039*	79.4	1222	.066
R5819	Teneriffe	.7037*	25.4	1146	.022
R5832	Madeira	.7032*	23.3	640	.036
	Average	.7035			

N Normalized to $Sr^{86}/Sr^{88} = .1194$

* Measured Sr^{87}/Sr^{86} ratios

Tristan da Cunha. A trachyandesite and a leucite trachybasalt from Tristan da Cunha have Sr^{87}/Sr^{86} ratios of .7053 and .7058 respectively (Table 15). Both rocks are greatly enriched in both rubidium and strontium in comparison with the subalkaline ridge basalts although rubidium is significantly more enriched in late magmatic differentiates. Both Sr^{87} regression lines (Figure 3) fall considerably short of 4.5 billion years.

From the recent ages of these samples it is apparent that the high Sr^{87}/Sr^{86} ratios are due not to rubidium decay subsequent to basalt formation, but to rubidium concentration relative to strontium in the source region of the upper mantle at an earlier period in earth history. These basalts would have to be at least 300 to 800 million years old for the Sr^{87}/Sr^{86} ratio to have grown from the average oceanic subalkaline basalts to the present value presuming the alkali magma source to have the same isotopic compositions as the subalkaline oceanic basalts. Sample R6103 is from a 1961 eruption and the average of all potassium-argon ages for the basalts of Tristan is one million years (Miller, 1964).

The strontium isotope data are in close agreement with the results obtained by Gast, Tilton, and Hedge (1964) for Gough Island located 230 miles south-southeast of Tristan da Cunha.

Analyses of a Boulder Dredged from 22°56'N 46°35'W.

Samples R5978, R5979, R5980 are considered separately from the other dredge basalts because they are from a basalt boulder that is considerably altered. The boulder is a high alumina porphyritic basalt with tholeiitic affinities, described and sketched by Cifelli (1965) with petrographic description and chemical analyses by Nicholls, Nalwalk, and Hays (1964). These analyses are reproduced in Appendix A. R5978 is a sample of the glassy margin, R5979 of an intermediate region, and R5980 of the core. From the high Fe_2O_3/FeO ratio and from the color and opacity of the ground mass, Nicholls, Nalwalk, and Hays (op. cit.) conclude that the groundmass has experienced considerable alteration, most probably by sea water. The strontium isotope ratios (Table 13) reported here tend to support this conclusion. All three samples have Sr^{87}/Sr^{86} ratios (.7055 - .7066) higher than the highest values yet reported for oceanic dredge samples. Contamination by sea water strontium (Sr^{87}/Sr^{86} = .7090 ± .0005, Faure, et al, 1965; corrected to standard $SrCO_3$ Sr^{87}/Sr^{86} = .7081) can account for these high ratios. The analyses for total strontium and rubidium reveal a pronounced strontium decrease and a very slight rubidium increase from the core to the glassy margin (Table 14). However, because of the porphyritic nature of the sample, it would be a mistake to conclude, just from the rubidium and strontium results, that strontium leaching has occurred.

The Sr^{87} regression lines (Figure 3), although displaced slightly from the regression lines for the other mid-Atlantic Ridge samples, do not have significantly different slopes.

The concentration of strontium in the glassy margin of this boulder (R5978) is the same as the average obtained for the other subalkaline basalts from the ridge whereas the interior of the sample (5980) shows a two- to three-fold enrichment. There is no corresponding enrichment of rubidium.

P. M. Hurley (personal communication) suggests that the enrichment of strontium in the center of the boulder possibly may be due to the distillation of sea water which penetrated the glassy margin while the interior was still hot shortly after the boulder was erupted. Subsequent leaching of the sea water-introduced strontium could account for the observed strontium concentration gradient.

Pacific Ocean

Subalkaline Dredge Basalts. Rubidium and strontium abundances and strontium isotopic compositions for three basalts dredged from the East Pacific Rise and four dredged from the Molokai fracture zone are reported in Tables 16 and 17.

The Sr^{87}/Sr^{86} ratios for all seven samples are in the range .7027 to .7038 (averaging .7033) which is comparable

Table 16

Strontium Isotopic Composition of East Pacific Rise and Molokai Fracture Zone Samples

Sample No.	$Sr^{87}/Sr^{86}\Big\|^{N}_{C}$	$Sr^{87}/Sr^{86}\Big\|^{N}_{M}$	Final $Sr^{87}/Sr^{86}\Big\|^{N}$ [1]
East Pacific Rise			
R5950	.7027 (2)[2]		.7027
R5951	.7036		.7036
R5952	.7035		.7035
Molokai Fracture Zone			
R5964	.7034 (2)[2]	.7034	.7034
R5965		.7033	.7033
R5966	.7039	.7032 (C)[3]	.7032
		.7031 (S)[3]	
R5967	.7048 (2)[2]	.7039 (C)[3]	.7038
		.7036 (S)[3]	
		Average	.7033

N Normalized to $Sr^{86}/Sr^{88} = .1194$

C Calculated ratio

M Measured ratio

[1] All $Sr^{87}/Sr^{86}\Big|^{N}$ ratios corrected to E and A standard $SrCO_3 = .7081$

[2] Number in parentheses indicates number of analyses

[3] Letter in parentheses indicates mass spectrometer used:

(C) Connie

(S) Sally

Table 17

Strontium and Rubidium Concentrations in East Pacific Rise and Molokai Fracture Zone Basalts

Sample No.	Sr ppm	Rb ppm[1]	Rb/Sr
East Pacific Rise			
R5950	113.3, 114.3 > 113.8	0.41	.0036
R5951	110.5	6.77	.0612
R5952	140.7	0.69	.0049
Molokai Fracture Zone			
R5964	114.3, 115.2 > 114.8	2.50, 2.46 > 2.48	.0016
R5965	132.8, 133.2 > 133.0	2.61, 2.61 > 2.61	.0196
R5966	122.0, 121.5 > 121.8	2.65, 2.62, 2.67 > 2.64	.0217
R5967	128.3, 126.0 > 127.2	2.87, 2.90 > 2.88	.0227
Average	123.1 ppm	2.64 ppm	.0222

[1]Corrected for blank contamination .048 ppm

to the range and average obtained for the mid-Atlantic Ridge samples. The average rubidium and strontium abundances are 2.64 ppm and 123.1 ppm respectively and the average Rb/Sr ratio is .0222.

The Molokai samples are much more uniform isotopically and in rubidium and strontium abundances than the East Pacific Rise samples. Admittedly, this may be a sampling feature since the three Rise samples are from widely separated locations whereas the Molokai samples are from a one locality.

Strontium-87 regression lines for these samples are illustrated in Figure 5 . With the exception of East Pacific Rise Sample R5951, which has a Rb/Sr ratio of .061, all the regression lines project beyond 4.5 billion years.

The average concentration of strontium in these basalts is 123.1 ppm and of rubidium, 2.641 ppm.

Hawaiian Islands. Eighteen samples representative of the many basalt types found in the Hawaiian Islands have Sr^{87}/Sr^{86} ratios in the range .7027 to .7048 (Table 18). Their rubidium and strontium concentrations, as well as the potassium abundances calculated from the chemical analyses, are reported in Table 19.

On the basis of the Sr^{87}/Sr^{86} ratios, the basalts may be divided into three groups:

1. The tholeiites which are characterized by high Sr^{87}/Sr^{86} ratios. They range from .7038 to .7048 and average .7045.

FIGURE 5

Sr^{87} Regression Lines for East Pacific Rise and

Molokai Fracture Zone Basalts

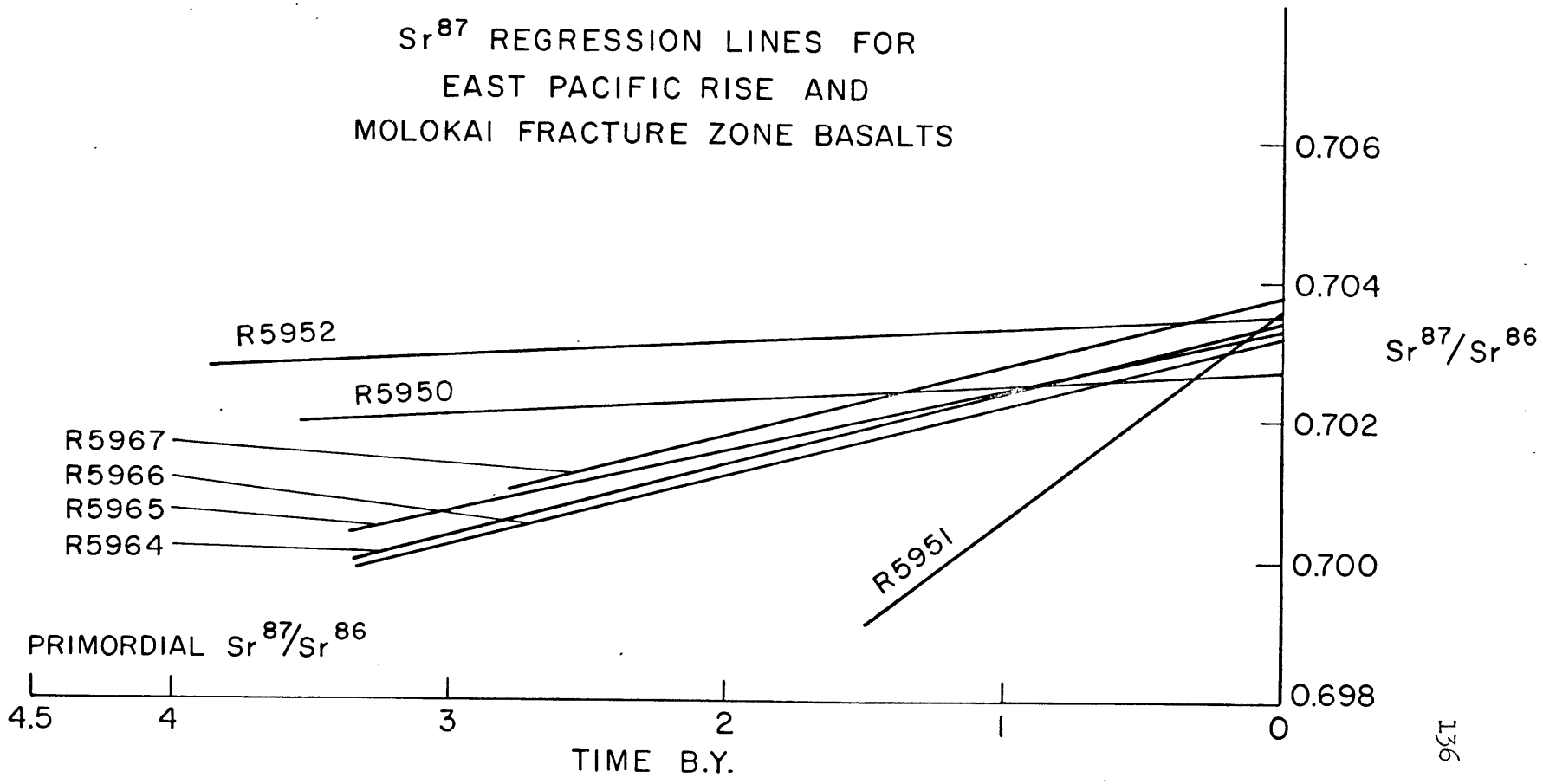

Sr87 REGRESSION LINES FOR
EAST PACIFIC RISE AND
MOLOKAI FRACTURE ZONE BASALTS
R5952
R5950
R5967
R5966
R5965
R5964
R5951
0.706
0.704
0.702
0.700
0.698
Sr87/Sr86
PRIMORDIAL Sr87/Sr86
4.5
4
3
2
1
0
TIME B.Y.

Table 18

Strontium Isotopic Composition of Hawaiian Basalts

Sample Number		Sr^{87}/Sr^{86} N C	Sr^{87}/Sr^{86} [1]
R6321	Hawaiite	.7035	.7043 (2)
R6322	Basanitoid	.7028	.7033 (2)
R6323	Tholeiite	.7038	.7041 (2)
R6324	Nepheline basalt	.7030	.7031 (3)
R6325	Alkaline-olivine basalt	.7030	.7040 (2)
R6326	Trachyte	.7033	.7043 (2)
R6327	Melilite-nepheline basalt	.7027 (2)[2]	.7030 (2)
R6328	Tholeiite	.7048	
R6329	Nepheline-melilite basalt	.7043 (2)	
R6330	Linosaite	.7037	
R6331	Nepheline basanite	.7035	
R6332	Ankaramite	.7040	
R6333	Hawaiite	.7044	
R6334	Mugearite	.7046	
R6335	Andesite	.7031	
R6336	Tholeiite	.7048	
R6337	Diabase	.7043	
R6338	Tholeiite	.7046	

[1] Data from Powell, et al (1965) relative to standard $Sr^{87}/Sr^{86} = .7085$

[2] Figures in parentheses indicate number of analyses.

N Normalized to 86/88 = .1194

C Calculated ratio.

Table 19

Strontium and Rubidium Concentrations of Hawaiian Basalts

Sample Number	K ppm*	Sr ppm	Rb ppm	Rb/Sr	K/Rb
R6321	15100	1260	36.6	.029	413
R6322	4980	539	20.6	.038	242
R6323	3070	290	5.73[1]	.020	536
R6324	9960	1303	36.2	.028	275
R6325	6970	419	21.4	.051	326
R6326	40900	54.5	113.8	2.09	359
R6327	14780	1759	46.5	.038	318
		1746	46.7	.037	
R6328	1245	329	2.18[1]	.007	572
R6329	7550	2155	20.9	.010	361
		2145			
R6330	8460	992	28.9	.029	293
R6331	7720	635	22.9	.036	337
R6332	3480	453	16.3	.036	214
R6333	13280	1107	40.2	.036	331
R6334	22580	1061	58.4	.055	387
R6335	10790	908	28.3	.031	381
R6336	1826	396	.495[1] .504[1] .463[1]	.001	3749
R6335	4980	346	5.99[1]	.017	830
R6338	2905	432	6.43[1]	.015	452

*Calculated from chemical analyses

[1]Corrected for rubidium blank contamination .048 ppm

2. The nepheline melilite basalts which, with one exception, tend to have low Sr^{87}/Sr^{86} ratios (.7027 - .7030).

3. The alkali series basalts include the trachyte. Their Sr^{87}/Sr^{86} ratios range from .7028 to .7046.

A correlation of Rb-Sr and La abundances presented in the appendix, also points out these groupings with the exception that the trachyte is placed in a fourth group. These groupings tend to support the conclusion of Powell, et al (1965) that there is a slight but significant decrease of radiogenic Sr^{87} with decreasing silica content. This may be due to a decreasing Rb/Sr ratio with depth in the source region.

Kushiro and Kuno (1964) conclude from theoretical studies of the forsterite-enstatite-silica system that undersaturated basalts can be derived from greater depths than either tholeiitic or alkaline basalts. This is due to the pressure effect upon the melting behavior of enstatite which at low pressures melts incongruently giving SiO_2 and Mg_2SiO_3 in the melt. At high pressures it melts congruently and no SiO_2 is formed. Similar results are shown for the partial melting of garnet periodite.

Strontium-87 regression lines for the Hawaiian basalts are illustrated in (Figures 6,7 and 8). The tholeiitic basalts, like the subalkaline basalts from the oceanic ridges, extend back beyond 4.5 billion years. All the other samples extend

FIGURE 6

Sr^{87} Regression Lines for Hawaiian Tholeiitic Basalts

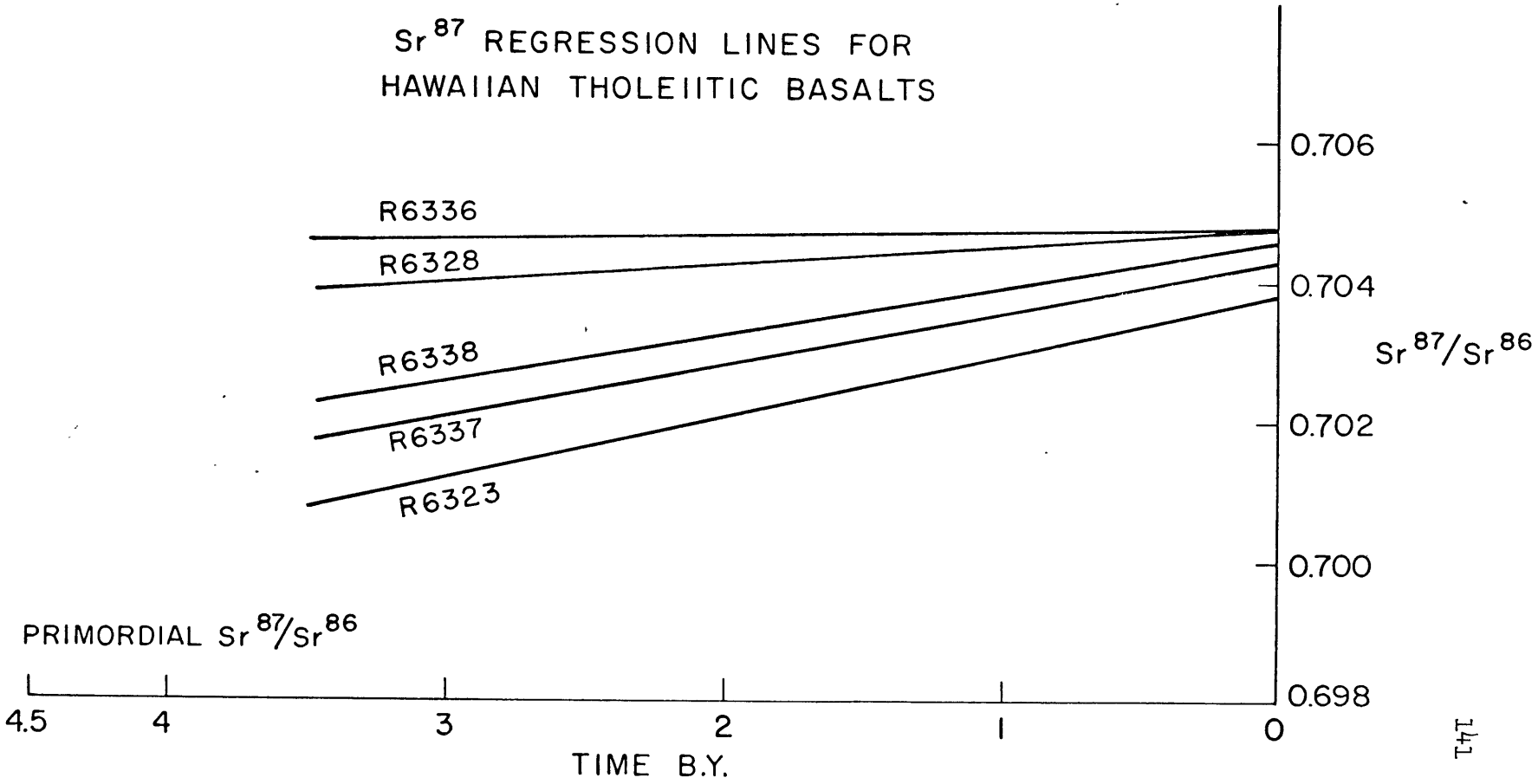

Sr 87 REGRESSION LINES FOR
HAWAIIAN THOLEIITIC BASALTS
R6336
R6328
R6338
R6337
R6323
0.706
0.704
0.702
0.700
0.698
Sr 87/Sr 86
PRIMORDIAL Sr 87/Sr 86
4.5
4
3
2
1
0
TIME B.Y.

FIGURE 7

Sr^{87} Regression Lines for Hawaiian Alkali Series Basalts

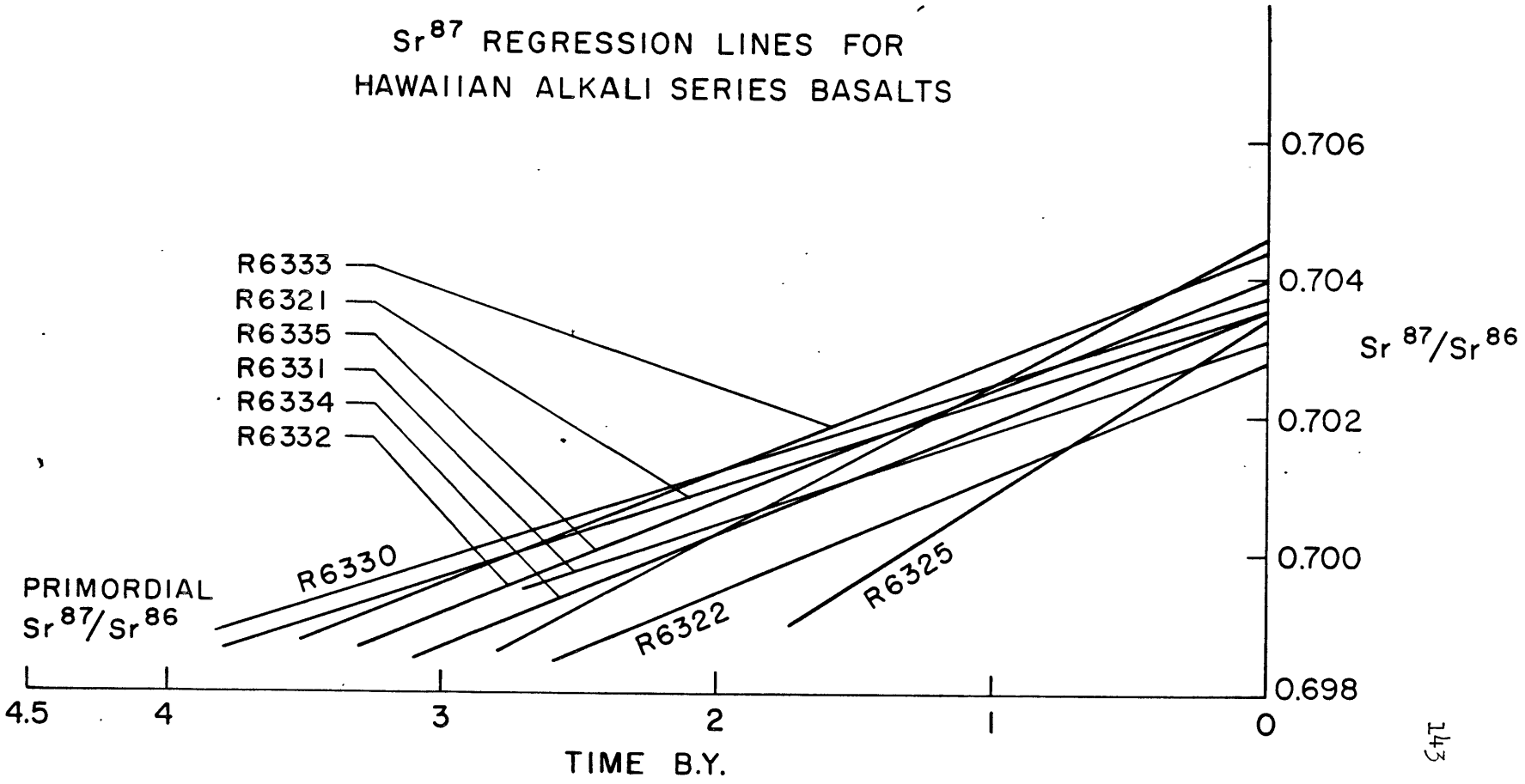
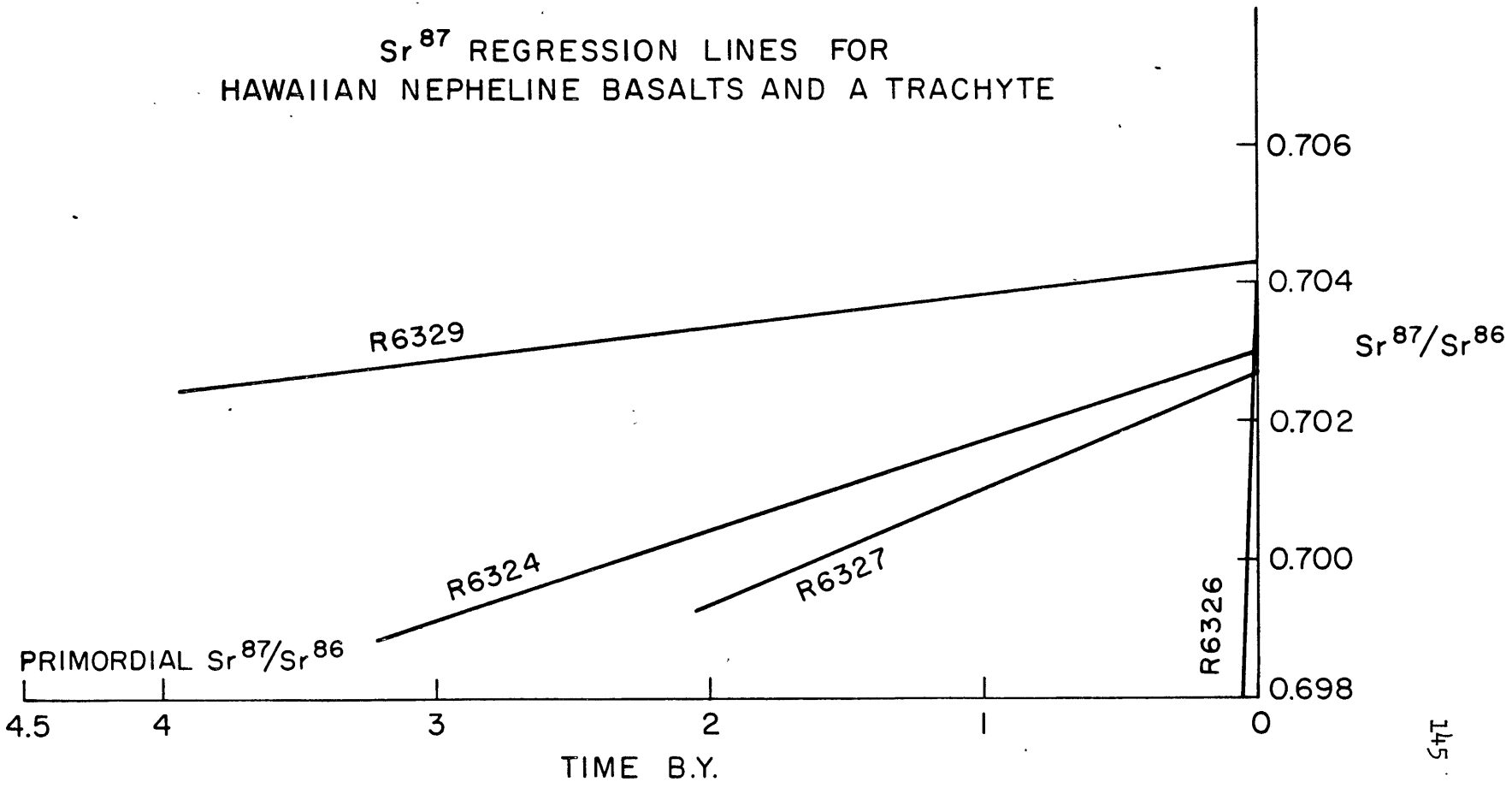

Sr87 REGRESSION LINES FOR
HAWAIIAN ALKALI SERIES BASALTS
R6333
R6321
R6335
R6331
R6334
R6332
R6330
R6322
R6325
PRIMORDIAL
Sr87/Sr86
0.706
0.704
0.702
0.700
0.698
Sr 87/Sr 86
4.5
4
3
2
1
0
TIME B.Y.

FIGURE 8

Sr^{87} Regression Lines for Hawaiian Nepheline Basalts

and a Trachyte


Sr 87 REGRESSION LINES FOR
HAWAIIAN NEPHELINE BASALTS AND A TRACHYTE
0.706
0.704
0.702
0.700
0.698
Sr 87/Sr 86
R6329
R6324
R6327
R6326
PRIMORDIAL Sr 87/Sr 86
4.5
4
3
2
1
0
TIME B.Y.

back to 4.5 billion years or fall short of it. The rubidium enrichment in the trachyte, relative to strontium, is so great that the regression line slope is approaching infinity.

It is important to note that the Hawaiian tholeiites have about a three-fold enrichment in both strontium and rubidium over the subalkaline ridge basalts although the Rb/Sr ratios are almost identical. The Sr^{87}/Sr^{86} ratios for the Hawaiian tholeiites as a group are consistently higher than the same ratio for the subalkaline ridge basalts.

With one exception, the K/Rb ratios (Table 19) for the Hawaiian tholeiites occur in the range 450 to 800 and are all lower than the K/Rb ratios in the subalkaline dredge basalts. The exception, R6336 has an unusually high K/Rb ratio due to an extremely small rubidium concentration.

The K/Rb ratios for the alkaline and nepheline-bearing series lie in the range from about 250 to 400 with an average of 326. There is no systematic decrease of K/Rb ratios with increasing K_2O.

Summary

A number of important observations can be made from the results of this investigation.

1. The subalkaline basalts dredged from the ocean floors and ridges have low concentrations of potassium, rubidium, and strontium in comparison with the

subalkaline and alkaline island basalts. The subalkaline island basalts such as the Hawaiian tholeiites have a two-to three-fold enrichment of both rubidium and strontium over their ocean floor and ridge counterparts. The potassium abundances are also slightly higher in the island tholeiites.

2. The Rb/Sr ratios for the subalkaline basalts (island and ridge) are low (about .01) and when the Sr^{87} regression lines are drawn, they project back beyond 4.5 billion years at the primordial Sr^{87}/Sr^{86} ratio.

3. The oceanic alkaline basalts are all enriched in rubidium relative to strontium such that their Rb/Sr ratios are considerably greater than for the subalkaline basalts. The Sr^{87} regression lines for the alkaline basalts all fall short of 4.5 billion years at the primordial Sr^{87}/Sr^{86} ratio.

4. The Sr^{87}/Sr^{86} ratios for all fresh oceanic basalts occur in the range .702 to .706 with the following averages noted for the localities sampled (number of analyses in parentheses):

East Pacific Rise and

Molokai Fracture Zone .7033(7)

Mid-Atlantic Ridge	.7037(8)
Canary Islands and Madeira	.7035(7)
Tristan da Cunha	.7055(2)
Hawaiian Islands	.7038(18)

5. The Hawaiian basalts may be divided into three groups on the basis of their Sr^{87}/Sr^{86} ratios:

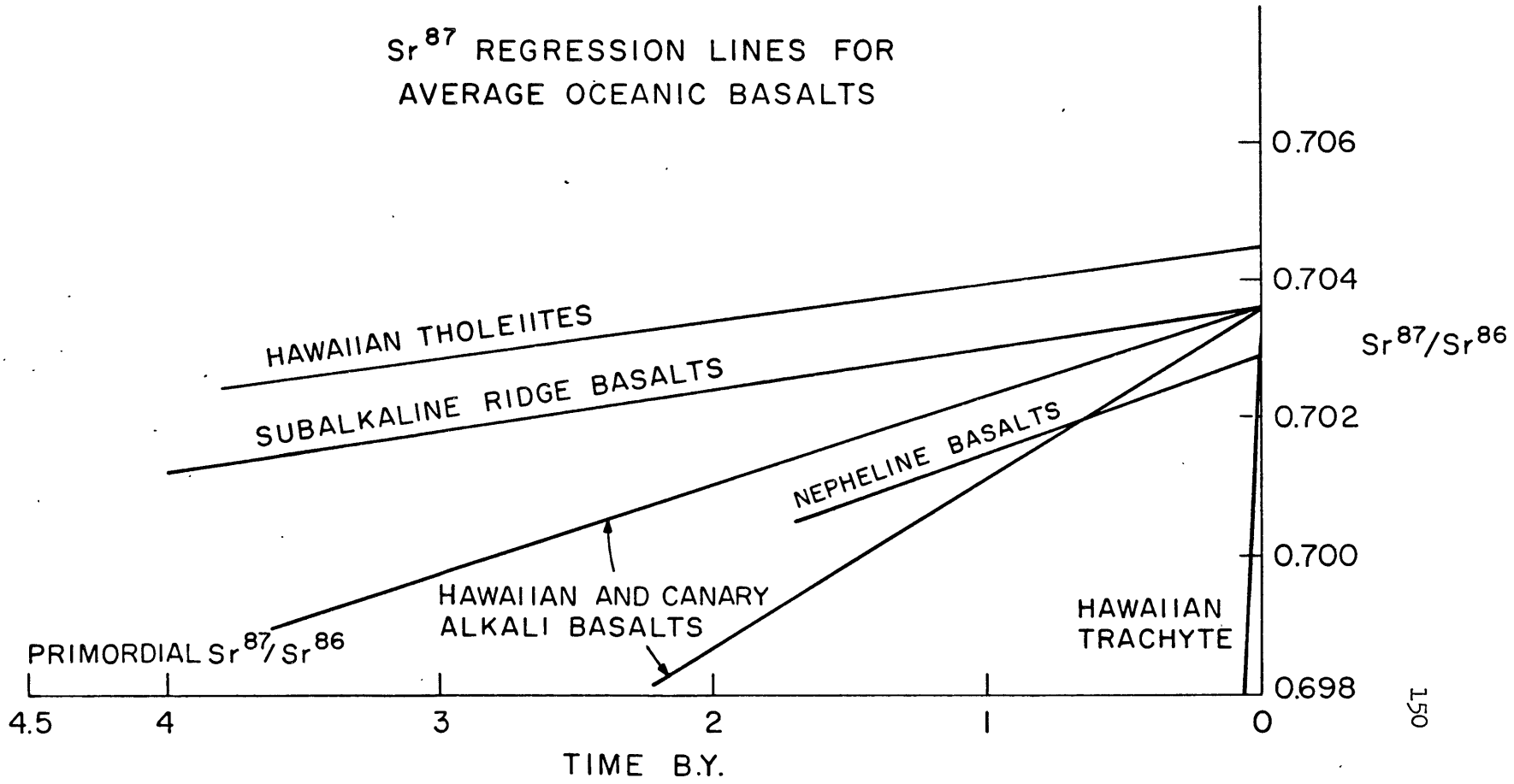
a) Tholeiites	.7045(5)
b) Nepheline melilite basalts	.7029(2)
c) Alkaline series and trachyte	.7036(10)

6. The K/Rb ratios for the subalkaline dredge basalts are variable, but in the range 550 to 3400 and are the highest of any terrestrial materials. The subalkaline basalts from the Hawaiian Islands have, with one exception, K/Rb ratios from 450 to 800. The alkaline basalts from the Hawaiian Islands and Tristan da Cunha have K/Rb ratios from 250 to 400. No systematic decrease of K/Rb ratios with increasing K_2O is noted in the alkaline basalts from the Hawaiian Islands.

A summary of the rubidium-strontium relationships in the samples is shown on the Sr^{87} regression diagram of Figure 9.

FIGURE 9

Sr^{87} Regression Lines for Average Oceanic Basalts


Sr^{87} REGRESSION LINES FOR
AVERAGE OCEANIC BASALTS
0.706
0.704
0.702
0.700
0.698
Sr^{87}/Sr^{86}
HAWAIIAN THOLEIITES
SUBALKALINE RIDGE BASALTS
NEPHELINE BASALTS
HAWAIIAN AND CANARY
ALKALI BASALTS
HAWAIIAN
TRACHYTE
PRIMORDIAL Sr^{87}/Sr^{86}
4.5
4
3
2
1
0
TIME B.Y.

CHAPTER IV

DISCUSSION

Geochemical Concepts and Definitions

Theory of Trace Element Behavior. Trace elements are defined as those elements which, because they are present in very low concentrations have chemical potentials too low for them to form their own phases. They are generally found in solid phases substituting for a major cation in the crystalline lattice, occupying a defect in the lattice, or adsorbed on crystal surfaces from which they are relatively easily removed.

Extensive thermodynamic treatments of trace element behaviors in coexisting phases in geological situations are described by Ramberg and DeVore (1951), Ramberg (1952), Kretz (1959, 1960, 1961), McIntire (1963), Mueller (1964), and Irvine (1965) to name a few.

The chemical potential (μ_i) of a species (i) is defined as the change in Gibbs Free Energy per mole holding pressure, temperature, and the concentration(s) of any other specie(s) (j) constant or, in the standard notations of chemical thermodynamics,

$$\mu_i = (\partial G/\partial n)_{P,T,n_j \neq n_i} \qquad (1)$$

For an ideal solution, which, by definition has no heat of mixing and the partial volumes are independent of concentration, the chemical potential of a trace element can be expressed in the following manner:

$$\mu_i(P,T,x_i) = \mu_i^{\circ}(P,T) + RT\ell n\ x_i \qquad (2)$$

where $\mu_i^{\circ}(P,T)$ is the standard chemical potential for the pure species (i) and is a function only of temperature and pressure. $RT\ell n\ x_i$ is an entropy term with R the gas constant and x_i the concentration of i (usually as the mole fraction).

In geological processes, the ideal situation rarely prevails and another term, the activity of coefficient γ_i, is introduced to account for the non-ideality.

Now,

$$\mu_i(P,T,x_i) = \mu_i^{\square}(P,T) + A\ell n\ \gamma_i x_i \qquad (3)$$

where $\mu_i^{\square}(P,T)$ is the hypothetical Gibbs Free Energy per mole for pure solute (i) at infinite dilution obeying Henry's Law. $A\ell n\ \gamma_i x_i$ is the energy due to the configurational entropy term which varies with the number of substitional sites available. When only a single site is available, A = RT. The activity coefficient γ_i is expressed in terms of the activity or thermodynamic concentration of the species by the following expression

$$\gamma_i x_i = a_i \qquad (4)$$

where a_i is the activity of the species (i). By convention, $\gamma_i \rightarrow 1$ as $x_i \rightarrow 0$.

The behavior of a minor element in magmatic processes is by no means well understood however, it may be stated that

each trace element partitions itself in a characteristic manner between coexisting solid and liquid phases. Providing equilibrium is maintained, the chemical potential of a trace element (i) in the solid phase (s) is equal to its chemical potential in the liquid phase (ℓ) or,

$$\mu_i^s = \mu_i^\ell \tag{5}$$

Therefore, from (3)

$$\mu_i^{\circ s}(P,T) + A\ell n\ \gamma_i^s x_i^s = \mu_i^{\circ \ell}(P,T) + A\ell n\ \gamma_i^\ell x_i^\ell \tag{6}$$

and solving for $\frac{x_i^s}{x_i^\ell}$ gives

$$\frac{x_i^s}{x_i^\ell} = \frac{\gamma_i^\ell}{\gamma_i^s}\ e^{\left(\frac{\mu_i^{\circ \ell}(P,T) - \mu_i^{\circ s}(P,T)}{RT}\right)} = d \tag{7}$$

where d is the partition coefficient for this single solid phase. When $d < 1$ the liquid is enriched in the trace element.

When x_i is infinitely dilute and Henry's Law holds,

$$\gamma_i^\ell \rightarrow \gamma_i^s \rightarrow 1 \text{ and}$$

$$d = \frac{x_i^s}{x_i^\ell} = \text{constant}$$

for a single-solid phase (s). When more than one solid phase is present, the effective partition coefficient D of a trace element is the summation of the concentrations of the trace element in each phase times the proportion of that phase divided by the concentration of the trace element in the liquid or,

$$D = \sum_{\alpha=1}^{n} \frac{P^{\alpha} x_i^{\alpha}}{x_i^{\ell}} \qquad (8)$$

where P^{α} is the proportion of solid-phase α and x_i^{α} is the concentration of i in α.

The pressure and temperature dependence of d may be obtained from (7) which may alternatively be written

$$\ell n\ d(P,T) = \ell n \frac{x_i^{s}}{x_i^{\ell}} = \frac{\mu_i^{\square\,\ell}(P,T) - \mu_i^{\square\,s}(P,T)}{RT} \qquad (9)$$

when x_i is infinitely dilute. Differentiating with respect to P and T gives

$$d\ell n\ d(P,T) = \left(\frac{\partial \ell n\ d}{\partial T} \right)_P dT + \left(\frac{\partial \ell n\ d}{\partial P} \right)_T dP \qquad (10)$$

$$d\ell n\, d(P,T) = \left(\frac{\partial \left(\frac{\mu_i^{\circ\, \ell}(P,T) - \mu_i^{\circ\, s}(P,T)}{RT} \right)}{\partial T} \right)_P dT$$

$$+ \left(\frac{\partial \left(\frac{\mu_i^{\ell}(P,T) - \mu_i^{s}(P,T)}{RT} \right)}{\partial P} \right)_T dP \qquad (11)$$

But

$$\frac{\partial\, \mu_i^{\circ\, \alpha} / T}{\partial T} = \bar{H}_i^{o\,\alpha} \qquad (12)$$

where $\bar{H}_i^{o\,\alpha}$ is the partial molar enthalpy at infinite dilution in phase α

and

$$\frac{\partial \mu_i^{\circ\, \alpha}/T}{\partial P} = -\bar{V}_i^{o\alpha} \qquad (13)$$

where $\bar{V}_i^{o\alpha}$ is the partial molar volume at infinite dilution in phase α .

Substituting (12) and (13) in (11) gives

$$d\ell n\, d = \left(\frac{\bar{H}_i^{o\ell} - \bar{H}_i^{os}}{RT^2} \right) dT + \left(\frac{\bar{V}_i^{os} - \bar{V}_i^{o\ell}}{RT} \right) dP \qquad (14)$$

$$d\ell n\ d = \frac{\Delta \bar{H}^o}{RT^2}\, dT + \frac{\Delta \bar{V}^o}{RT}\, dP \qquad (15)$$

when the solid is composed of a single phase. When more than one solid phase is present, $\Delta \bar{V}^o$ and $\Delta \bar{H}^o$ terms must be written for each solid phase and the coexisting liquid as a function of the proportion of the phase in the solid, or,

$$d\ell n\ D = \sum_{\alpha=1}^{n} \frac{P^\alpha \Delta \bar{H}_i^{o\alpha}}{RT^2}\, dT + \sum_{\alpha=1}^{n} \frac{P^\alpha \Delta \bar{V}_i^{o\alpha}}{RT}\, dP \qquad (16)$$

where P^α is a proportionality factor of phase α.

At constant pressure,

$$d\ell n\ D = \sum_{\alpha=1}^{n} \frac{P^\alpha \Delta \bar{V}_i^{o\alpha}}{RT}\, dP \qquad (17)$$

or

$$D_2/D_1 = e^{\sum_{\alpha=1}^{n} \frac{P^\alpha \Delta \bar{V}_i^{o\alpha}}{RT} (P_2 - P_1)} \qquad (18)$$

At constant pressure,

$$d\ell n\ D = \sum_{\alpha=1}^{n} \frac{P^{\alpha} \Delta \bar{H}_i^{o\alpha}}{RT^2}\ dT \qquad (19)$$

or

$$D_2/D_1 = e^{\sum_{\alpha=1}^{n} \frac{P^{\alpha} \Delta \bar{H}_i^{o\alpha}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \qquad (20)$$

The pressure term is the most dominant term affecting the effective partition coefficient in the deep mantle (below about 500 km) since pressure determines what assemblage of phases is stable. It is probable that the ionic radius of a trace ion and the size of the site available to it become the dominant controlling parameters of trace element behaviors at high pressures (greater than about 100,000 bars). Above the transition zone (about 400 km), the temperature term begins to dominate and the valence and type of chemical bond may become more influential.

Upper mantle material is most likely a combination of three major phases: olivine, pyroxene, and pyrope. The proportion of these phases probably varies with depth but olivine

generally predominates. Analyses of the alpine-type ultramafics have shown that the amounts of trace elements accepted into the olivine structure are extremely small while the pyroxene-bearing ultramafics may contain slightly higher concentrations. Therefore, depending upon the relative proportion of the solid phases present, the absolute abundance of a trace component and its effective partition coefficient D can vary significantly. In the absence of experimental studies duplicating the assumed physical and chemical conditions in the mantle, it is difficult, if not impossible, to predict the value of the effective partition coefficient for a particular trace element or the magnitude of the changes it undergoes by changing the relative proportions of phases or by introducing new phases. It is possible, however, to estimate the ratio of the effective partition coefficients for two slightly dissimilar trace elements. Rubidium, for example, becomes enriched in the liquid phase of magmatic processes relative to strontium and the ratio of D_{Rb}/D_{Sr} is always less than unity. By the same argument, D_K/D_{Rb} is greater than unity.

Since the effective partition coefficient for any trace element is dependent upon the type and proportion of major phases present and is a characteristic of that element, the ratios of two trace elements may change significantly with

depth in the mantle in response to changing chemical or physical conditions.

The processes by which the earth has differentiated have produced substantial enrichments of trace components in the upper mantle and crust. The magnitude of these enrichments is difficult to estimate. Near the top of the upper mantle there is probably significant enrichment of trace components yet the absolute abundances cannot be great considering their concentrations in subalkaline oceanic basalts. In cases of extreme differentiation such as multiple-zone refining (Harris, 1957) the maximum concentration of a trace element in upper mantle material is limited by the number of passes and by the location of the material in the column. The introduction of new phases in response to changing physical conditions may produce discontinuities in the concentration curve.

Behavior of Rubidium and Strontium. In all but a few geological circumstances, rubidium and strontium behave as trace elements and may be studied theoretically using the thermodynamic relations of dilute solutions. Very rarely, in sedimentary or hydrothermal environments, these elements may behave as major cations and strontium may form its own mineral phases such as strontianite or celestite. However, in the processes of basalt magma generation from upper mantle material these elements occur in concentrations so small that they may be

treated as obeying Henry's Law without introducing significant errors.

In the continuous differentiation of the mantle, rubidium and strontium, because of their large ionic radii relative to the major cations, are concentrated in the fluid phases if such exist. The upward movement of the fluids sweeps these trace elements towards the surface where they are concentrated in the upper mantle and crust.

The upper mantle zone of interest in magma generation is that below about 40 km and extending to about 400-600 km. Seismic activity associated with magma eruption in the Hawaiian Islands (Eaton and Murata, 1960) suggests that the basalt magmas are derived from depths of about 60 km and may have been generated there. The major silicate phases that are stable in this region are believed to be pyroxene, olivine, pyrope, and jadeite.

The effective partition coefficients for both rubidium and strontium (D_{Rb} and D_{Sr}) are both very much less than unity in the basalt source regions. A small degree of partial melting removes essentially all of the rubidium and strontium from the source material and concentrates it in the liquid phase.

Strontium behaves in a manner similar to calcium because it is the only major cation with the same charge and a similar ionic radius. The difference in their ionic radii (using values reported by Ahrens, 1965) is about 15% which is about the maximum

that still permits diadochic substitution.

Under the physical conditions present in the upper mantle, calcium garnet (pyrope) and calcic pyroxene are not major acceptor phases for strontium even though they are stable. Consequently, D_{Sr} is less than unity in the upper mantle and the chemical potential of strontium builds up in the fluids as they migrate towards the surface.

Rubidium behaves in a manner similar to strontium in the upper mantle. It has an ionic radius comparable to that of potassium (Rb = 1.45Å, K = 1.33Å) and tends to follow that element in magmatic processes resulting in its concentration in the final differentiation products.

As the fluid phases move towards the surface from depth where forsterite is the dominant phase, both Rb and Sr are concentrated in the liquid phase and the Rb/Sr ratio remains fairly constant. However, the proportion of pyroxene increases towards the surface and, although the concentration of rubidium in pyroxene and olivine are about the same, the concentration of strontium in pyroxene is about ten times higher in pyroxene. Therefore, the ratio D_{Rb}/D_{Sr} increases slowly with decreasing depth as the relative abundance of pyroxene increases but will always remain less than one.

In the low pressure regimes of the crust, calcic plagioclase is stable and crystallizes from the rising fluids. When this happens, strontium follows calcium into the plagioclase

lattice and, to a lesser extent, the diopside lattice. D_{Sr} is greater than one. The effective partition coefficient for rubidium meanwhile remains less than one and this element continues to be concentrated in the liquid phase. Consequently the Rb/Sr ratio increases rapidly and continues to increase with differentiation until potassium phases appear.

The Differentiation of the Earth

Introductory Statement. Although the results of this investigation in themselves do not establish the general history of differentiation in the earth, they add support to a complex development that involves great inhomogeneities at depth in the mantle akin to those at the surface.

The Composition of the Primitive Earth. Numerous lines of evidence, which are recently reviewed by Ringwood (1966a), suggest that the primitive earth had a composition comparable to the chondritic meteorites with respect to the major non-volatile elements.

It was first suggested by Urey (1953) that the carbonaceous chondrites were the closest approach to the primitive material of the solar system. Later, others (Mason, 1960; Ringwood, 1961) supported this suggestion and it is now a generally accepted feature of most earth models.

Detailed chemical studies of the carbonaceous chondrites uncovered major differences which are believed due to varying intensities of thermal metamorphism. On the basis of degree of oxidation and abundance of highly volatile elements, three groupings were noted: Type I carbonaceous chondrites which are the most highly oxidized and contain the greatest abundances of the highly volatile elements, and Types II and III which are increasingly depleted in the volatile elements and, apparently, have been subjected to increasing intensities of thermal metamorphism.

One of the more important features of the carbonaceous chondrites is the presence of iron entirely in the oxidized state. Ordinary chondrites have considerable amounts of metallic iron which indicates that they have been exposed to high temperature reducing conditions.

It has been inferred from geophysical evidence that the earths' core is composed of a mixture of iron, nickel, and probably silicon (MacDonald and Knopoff, 1958; Ringwood, 1959; Birch, 1964) in the metallic state. There is an inferred disequilibrium between the core and overlying silicate phases of the lower mantle (Ringwood, 1960, reviewed in 1966a). Also in a review article, Urey (1966) notes that there is a definite fractionation of iron relative to silicon in chondritic meteorites. Evidently then, the material that formed the earth and

and meteorites was, at some stage, exposed to high temperature reducing conditions but that the silicate and metal phases were quickly separated so that equilibrium was not established.

Further evidence for a high temperature stage early in the earth's history is indicated by the depletion of the alkali metals in the crust and upper mantle.(Gast, 1960). The loss of these volatiles is one of the major features which must be explained by a satisfactory earth model.

It seems reasonable to assume that the primitive earth had a chemical composition similar to the Type I carbonaceous chondrites after the most volatile elements are removed. Subsequent heating was responsible for the melting of iron, nickel, and some silicon and their reduction to the metallic state.

Single and Multistage Earth Models. Currently there are two principal hypotheses on the earth's formation and early history. One is built around a single stage development from primitive material of the solar nebula and the other around a multistage development. Each model has its strong and weak points and many observed phenomena cannot yet be adequately explained by either.

The single-stage model, strongly supported and recently reviewed by Ringwood (1966a), has the earth formed directly by accretion from the primitive gas-dust cloud of the solar nebula. Intense heating in the later stages of accretion, due to the release of the impact energy of the accreting planetesimals, resulted in high temperature reducing conditions near the surface while the interior remained relatively cool. Reduction of iron, nickel, and possibly, some silicon as well as the loss of volatile elements occurred in the near surface material. The build-up of surface temperatures was aided by the insulating effect of the primitive atmosphere. The accumulation of a gravitationally unstable layer of high density liquid metals near the surface followed with the gradual infall of these phases towards the center of the earth and resulted in the production of the protocore. Extensive, but not necessarily complete, melting or silicate phases resulted from the release of gravitational energy due to this process.

The multi-stage model, the strongest proponent of which is Urey (see review article, Urey (1966)), but which finds support from Wood (1962), Anders (1963), and many others, suggests that primary lunar-size objects were first formed in the solar nebula. Metal reduction and subsequent loss of the most volatile elements was the result of heating in this stage. Subsequent

collisions between the primary ojects caused them to break up but some of their fragments later accreted to form the terrestrial planets. Primitive atmospheres formed around the primary objects were lost in the collisions and the primitive earth did not have a major atmosphere developed in its early stages.

One of the major objections to the multistage model is that it does not adequately explain the loss of the alkali metals (specifically rubidium) from the earth early in its history. It is evident that a considerable amount of rubidium was lost relative to a hypothetical chondritic composition, yet less volatile compounds, particularly water, were retained to be later released by continuous degassing of the earth's interior.

On the other hand, one of the most attractive features of the multistage model is that there is complete removal of the primitive atmosphere developed in the early stages. Rubey (1951, 1955), Kulp (1951), and later Holland (1962) demonstrate that the earth's atmosphere and hydrosphere accumulated almost entirely by the slow degassing of the earth's interior through geologic time. If a primitive atmosphere was developed, it must have been almost completely removed in the early stages of the earth's development. Mechanisms for this removal are hard to visualize and this becomes one of the major weaknesses of the single-stage model.

Symmetrical Versus Asymmetrical Earth Models. For discussion of the results of this investigation we will outline two possible models of the earth's differentiation. These models will incorporate the ideas of many individuals but will divide them into two general groups.

Depending upon the degree of melting of the earth in the later stages of accretion and following core infall, two alternative models for the earth's gross structure may be visualized. One is radially symmetrical and the other asymmetrical. Subsequent differentiation of the mantle and the formation of the crust will be affected greatly by this early history.

If total, or extensive partial melting occurred following the infall of the core, where the energy release is about 600 calories per gram (Birch, 1965a,b), a radially symmetrical earth may result. The development of the crust and the upward migration of trace elements from such an earth would occur by the uniform removal of material from the mantle with little or no lateral movement. It should be noted here that if the primitive earth was not on a large scale homogeneous in the later stages of accretion, asymmetries could be retained in spite of almost complete melting.

The asymmetrical model could be developed in an initially homogeneous earth by the localization of the infall of the core to a specific zone or zones in the manner suggested by Elsasser (1963). If the rate of infall was sufficiently slow, melting

of silicate phases would be restricted to the regions of infall while the remainder of the "mantle" remained relatively cool. Magmas produced by this process were extruded to form basalt plates overlying the zones of infall. These plates may have been the continental nuclei. The mantle material underlying the plates would be the residuum remaining following the melting event and would be depleted in the trace elements. Mantle material away from the melted regions would retain its original trace element abundances.

The disequilibrium between the core and the mantle, the selective retention of some volatile elements and not others, and the asymmetrical distribution of the continents and oceans strongly favor a complex model for earth differentiation. A model in which the primitive earth was not a homogeneous mixture and in which differentiation did not proceed uniformly but asymmetrically, more effective in some zones than in others, is suggested. Such a model would help to explain the retention of volatiles in the primitive earth which are required for the later development of the atmosphere and hydrosphere.

In continuing with these two possible, but contrasting, models, we may tie mantle instability and continuing convection to one and mantle stability to the other. A symmetrical model does not preclude the possibilities of convection in the mantle. The asymmetric has an early continental plate overlying region

of the upper mantle depleted in trace elements. Away from the continental plates the upper mantle remained relatively enriched in trace elements. These enriched regions, which later become the oceanic areas, were unstable due to slow heating from the decay of long-lived radionuclides, and developed into the upward limb of a convection cell. Trace elements, alkalis, and Al_2O_3 brought to the surface in these areas were swept laterally to the downsinking limb of the convection cell where, because of their low densities, they remained at the surface and were added to the continental plates already there. In this manner the continents thickened and grew. These processes continued from the time of core separation until the present and continually added younger material to the edges of the continental plates.

Rubidium-Strontium Relationships in the Earth

Important Specific Observations Concerning the Earth.

A self-consistent earth model must satisfy all observations, from any sources, which are accepted as being factual. Therefore, as a first step in considering the earth's history of differentiation important characteristics of the earth are enumerated.

1. The age of the earth, within small limits, is the same as the meteorite ages or about 4.55×10^9 years (Patterson, 1956), Murthy and Patterson, 1962).

2. The initial Sr^{87}/Sr^{86} ratio for the earth is established at about 0.698 from the Rb-Sr meteorite isochron (Herzog and Pinson, 1956; Gast, 1961, 1962; Pinson, et al, 1965; Shields, Pinson and Hurley, 1966; Murthy and Compston, 1965).
3. The Rb/Sr ratio for the earth is significantly different from the chrondritic meteorites (Gast, 1960).
4. The sea water strontium Sr^{87}/Sr^{86} growth curve appears to start in the vicinity of 0.698 and increases exponentially to about .709 (Hedge and Walthall, 1963; Murthy, 1964; Faure, Hurley and Powell, 1965).
5. On the basis of initial Sr^{87}/Sr^{86} ratios, the majority of basalts at the earth's surface can be divided into two groups(Tables 20 and 21):
   a) Continental basalts $\left(Sr^{87}/Sr^{86}\right]_o$) = .705 - .707.
   b) Oceanic basalts $\left(Sr^{87}/Sr^{86}\right]_o$ = .702 - .705.
6. The continental basalts are characterized by:
   a) Not overly high Rb/Sr ratios.
   b) K/Rb ratios in the range 200-500.
   c) High trace element concentrations relative to oceanic basalts.
   d) Lead and uranium concentrations similar to the chrondrites.

Table 20

Isotopic Composition of Strontium in Recent Oceanic Basalts

	Standard $SrCO_3$	$Sr^{87}/Sr^{86}]_{observed}$
Indian Ocean		
Reunion (Hamilton, 1965b)	.7075	.7037(6)*
Reunion and Rodriquez (McDougall and Compston, 1965)	.7082	.7043(7)
Atlantic Ocean		
Iceland (Moorbath and Walker, 1965)	.7076	.7026(19)
(Hedge and Walthall, 1963)		.7025(2)
Ascension Island (Gast, Tilton and Hedge, 1964)		.7038(5)
(Faure and Hurley, 1963)	.7080	.7040(1)
Gough Island (Gast, Tilton and Hedge, 1964)		.7059(6)
Canary Islands (this study)	.7081	.7034(7)
Azores (Faure and Hurley, 1964)	.7080	.7058(1)
Tristan da Cunha (this study)	.7081	.7055(2)
Mid-Atlantic Ridge (Tatsumoto, Engel and Hedge, 1965)		.7024(3)
(Faure and Hurley, 1963)	.7080	.7032(1)
(this study)	.7081	.7037(8)
Pacific Ocean		
Hawaii (Lessing and Catanzaro, 1964)	.7085	.7049(15)
(Hedge and Walthall, 1963)		.7029(2)
(Powell, et al, 1965)	.7073	.7034(8)
(Faure and Hurley, 1963)	.7080	.7039(4)
(this study)	.7081	.7038(18)
(Hamilton, 1965a)		.7040(9)

Table 20 (Continued)

	Standard $SrCO_3$	$Sr^{87}/Sr^{86}]_{observed}$
Western Pacific		
Samoean Islands (Faure and Hurley, 1963)	.7080	.7047(3)
Mariana Islands (Pushkar, 1966)	.7083	.7038(5)
Izu Islands (Pushkar, 1966)	.7083	.7037(6)
New Zealand (Hedge and Walthall, 1963)		.7047(1)
East Pacific Rise		
(Tatsumoto, Engel and Hedge, 1965)		.7017(2)
(This study)	.7081	.7033(3)
Molokai Fracture Zone		
(this study)	.7081	.7035(4)

*Numbers of samples analyzed in parentheses

Table 21

Isotopic Composition of Strontium in Recent Continental Volcanic Rocks

	Standard $SrCO_3$	$Sr^{87}/Sr^{86}]_{observed}$
United States		
California rhyolite (Hedge and Walthall, 1963)		.7036(1)
California obsidian (Hedge and Walthall, 1963)		.7030(1)
Idaho basalt (Hedge and Walthall, 1963)		.7104(2)
Arizona basalt (Hedge and Walthall, 1963)		.7030(1)
New Mexico basalt (Hedge and Walthall, 1963)		.7037(1)
Colorado basalt (Hedge and Walthall, 1963)		.7048(1)
Italy		
(Hedge and Walthall, 1963)(andesite)		.7049(2)
Japan		
(Hedge and Walthall, 1963)(andesite)		.7052(1)
(Faure and Hurley, 1963)	.7080	.7051(3)
New Zealand		
(Hedge and Walthall, 1963)		.7047(1)
Central America		
(Pushkar, 1966)	.7083	.7040(3)
		Sr^{87}/Sr^{86} initial
Tertiary basalts		
Columbia River(Faure and Hurley, 1963)	.7080	.7035(1)
Deccan basalt (Faure and Hurley, 1963)	.7080	.7056(3)
Yellowstone basalt (Hedge and Walthall, 1963)		.7022(1)
Scotland Island of Skye (Moorbath and Bell, 1965)	.7090	.7058(12)

Table 21 (Continued)

	Standard $SrCO_3$	Sr^{87}/Sr^{86} initial
Triassic basalts		
Palisades (Faure and Hurley, 1963)	.7080	.7036(2)

7. The submarine "tholeiites" or subalkaline basalts of the oceanic group are characterized by:
   a) Low trace element concentrations (Engel, Engel and Havens, 1965).
   b) Low Rb/Sr ratios (about .01)(Tatsumoto, Hedge, and Engel, 1965; this study).
   c) High K/Rb ratios (about 800-3000) (Gast, 1965; Tatsumoto, Hedge and Engel, 1965; this study).
   d) Low U/Pb ratios (Tatsumoto, 1966).
   e) Low K_2O content.
8. Oceanic alkali basalts are characterized by:
   a) Enrichment of trace elements over the subalkaline basalts.
   b) The Rb/Sr ratios are higher than the Rb/Sr ratios for the subalkaline basalts.
   c) Similar Sr^{87}/Sr^{86} ratios to the subalkaline basalts so the Rb-Sr relationships are developed in recent times presumably during magma generation.
   d) U/Pb ratios are higher than the subalkaline basalts (Tatsumoto, 1966).
9. Rubidium/strontium ratios increase and K/Rb ratios decrease with differentiation.

10. Petrological observations.

    a) There are two distinct groups of volcanic rocks at the surface (continental and oceanic) which are non-uniformly distributed. The boundaries are those of the continents and are the so-called "andesite line".

    b) The mineralogical composition of the upper mantle is limited to high pressure silicate phases composed dominantly of MgO, FeO, and CaO.

    c) There is great enrichment of alkalis, Al_2O_3, and trace elements in the continental crust.

11. Geophysical observation:

    a) The silicate phases in the upper mantle are limited by measured seismic velocities which exceed 8km/sec. The mineralogy is limited to olivine, pyroxene, pyrope and possibly small amounts of jadeite and amphibole. Plagioclase is not stable in the upper mantle. The arguments pertaining to upper mantle mineralogy are recently reviewed by Ringwood (1966b).

    b) Gravity data indicate an average density for the continental crust which requires major proportions of feldspar or quartz.

12. Geophysical and physiographic studies of the oceanic ridges indicate that they are formed by the upwelling of material from depth.

13. Continental drift is a distinct possibility. Several independent sources suggest that the continents were together at one time. These include:

    a) Paleomagnetic data.

    b) The close fit of the continental coast lines especially the South American east coast and African west coast.

    c) Recent unpublished data on a close fit of age province boundaries between South American and Africa (Hurley, personal communication).

    d) Comparative geology and paleocology.

14. The favored mechanisms that would cause continental drifting are convection currents. If the mid-oceanic ridges are features produced over the upward rising limb of a convection cell, it is implied that elsewhere, on the downward limbs, there is downsinking of material.

A number of these "observations" which are incorporated into the present model, in particular, upper mantle convection cells and continental drift, are not universally accepted. However, the arguments in their favor are too strong to be dismissed lightly. It becomes then a matter of assessing the merits

of the objections to these processes and weighing them against the supporting evidence. As more and more data concerning the earth's crust and upper mantle regions are made available, it is increasingly evident that convection currents and continental drift are not only distinct possibilities, but must be considered as playing a major role in any model of a differentiating earth.

Rb/Sr Ratios in the Primitive Earth. The development of radiogenic strontium-87 in the earth is dependent upon the relative abundances of rubidium and strontium originally present. These abundances are by no means well known and, in a non-homogeneous primitive earth, would be variable, yet it is possible to make some rough estimation on the possible limits of the Rb/Sr ratio. In order to place limits upon this ratio it is necessary to follow the development of radiogenic strontium-87 in the crust and upper mantle. Crustal Rb/Sr ratios and the development of the present-day crustal Sr^{87}/Sr^{86} ratios may be studied by their measurements in surficial rocks. On the other hand, upper mantle Rb-Sr relationships must be inferred from their values in derivative basalt magmas.

It is well recognized that the earth's crust and upper mantle are depleted in rubidium relative to strontium in comparison with their ratio in chondrites. Selective volatization of rubidium in an early, high temperature stage of earth development is generally accepted to have been the primary reason for this deficiency. However, the very fact that oceanic and

atmospheric elements were retained locally in the earth demands that rubidium was also retained locally in its meteorite abundance relative to strontium.

The low initial Sr^{87}/Sr^{86} ratios (generally about .701) obtained for ancient Precambrian volcanic rocks place approximate lower limits upon the early Rb/Sr ratio in the parts of the upper mantle from where the magmas were generated. The growth of the Sr^{87}/Sr^{86} ratio from the primordial value of .698 to .701 in a period of about 1.5 to 2.5 billion years required a Rb/Sr ratio of .02 to .03 in the magma source regions.

Wide variations in the Rb/Sr ratio in the primitive earth are apparent which imply a rather complex and heterogeneous stage of early development in the earth and by doing so tend to favor an asymmetric model. In this model, the lowest Rb/Sr ratios (about .02) would occur in the regions of extensive melting where core infall was localized because rubidium volatization is more easily visualized there. The lowest absolute abundances of trace elements also occurred in this region. The highest Rb/Sr ratios (possibly comparable to the Type I carbonaceous chondrites where the Rb/Sr ratio is about 0.235 (Murthy and Compston, 1965)) were restricted to the mantle regions furthest removed from the regions of core infall. A complete graduation of Rb/Sr ratios existed in the intervening regions.

Rubidium-Strontium Relationships in Oceanic Basalts. The oceanic basalts analyzed in this study and those reported elsewhere in the literature have Sr^{87}/Sr^{86} ratios that fall within a very narrow range (.702 to .705 with minor exceptions). This indicates that the upper mantle source regions for these basalts must have been quite homogeneous for much of the earth's history with respect to their Rb/Sr ratio. In the discussion presented previously it was concluded that there was a slight variation with depth of the Rb/Sr ratio in the upper mantle. Presuming that this variation was initiated shortly after the formation of the core, it implies that the depth range for basalt magma generation is quite small or that the variation of the Rb/Sr ratio in this range is not great.

Variations in the Sr^{87}/Sr^{86} and lead isotope ratios for recent oceanic alkali basalts from widely separated localities (Gast, Tilton, and Hedge, 1964; Tatsumoto, 1966; this study) indicate that minor Rb/Sr (and U/Pb) heterogenities exist on a regional scale in the upper mantle. These lateral heterogeneities must have been produced fairly early in the earth's development.

The rubidium-strontium data are compatible with the development of regional heterogeneities in the young earth and present another argument in favor of the asymmetric earth model.

One of the principal objections of this study was the

Rb-Sr analysis of subalkaline basalts dredged from the ocean floors and ridges. The results obtained here show that these basalts are characterized by uniformly low abundances of both rubidium and strontium and very low (for basalts) Rb/Sr ratios (about 0?1). Other trace elements including K, U, and Th are also present in small concentrations (Tatsumoto, Hedge, and Engel, 1965; Engel, Engel, and Havens, 1965). The average $Sr\ 87/Sr^{86}$ ratio obtained for these subalkaline basalts is about .703, much too high to have been generated from material having a Rb/Sr ratio of .01 and an initial Sr^{87}/Sr^{86} ratio of .698. Evidently, the source material from which these basalts were derived had a higher Rb/Sr ratio in order to develop the necessary radiogenic Sr^{87}. Since that time, however, rubidium was removed from the system in preference to strontium.

If strontium was "enriched" relative to rubidium, and that is the case here even though the abundances of both elements are low, one of two situations must have prevailed. The strontium "enriched" system must have been residual in nature, or the partitioning behavior of rubidium and strontium between the basalt magma and coexisting solid phases must have changed drastically. In view of our present knowledge of the behavior of trace elements, the concentration of strontium over rubidium in a liquid phase, which is either residual from fractional

crystallization of a melt or a differentiate of partial melting, seems unlikely. It seems most probable, therefore, that the subalkaline oceanic basalt magmas have passed through a residual stage in their development. The term residual used here is meant to imply the last melting phases of partial melting which, in the case of complete melting, are also the first phases to crystallize upon cooling. In the latter case, the crystallization of pyroxenes and feldspars as early phases following olivine would account for an enrichment of strontium relative to rubidium in the solid phases.

In the previous section it was noted that the Rb/Sr ratio in what is now the oceanic upper mantle, could for a short time following the separation of the core in the asymmetric model, have been as high as the chondrite ratios. The continuous action of convection currents following the core infall could have brought about a gradual reduction of the ratio by the preferential removal of rubidium. In essence, the oceanic upper mantle became a residuum by the transfer of trace components, alkalis, and Al_2O_3 to the surface and then outward to the continental areas in a manner similar to that suggested by Patterson (1964).

The possibility that subalkaline basalt magmas were derivatives of a basic residual layer in the upper mantle previously suggested by Tatsumoto (1966) is further substantiated here. It does not appear reasonable, to this investigator,

that the subalkaline oceanic basalts were derived by the partial melting of upper mantle material unless the trace components, rubidium in particular, were previously removed. Partial melting without prior removal of rubidium would require two discrete periods of melting for the production of subalkaline magmas; one to remove the alkali components and the second to generate the subalkaline magma. This implies that considerable quantities of alkali- and trace-component-rich basalts were extruded in oceanic areas before subalkaline basalt magmas. This is a reversal of the tholeiite-alkali basalt relationships noted in the Hawaiian Islands. These observations therefore favor tha asymmetrical earth model with continuing convection.

The Sr^{87}/Sr^{86} ratios obtained for the Hawaiian Islands suite indicate that there is, on a small scale at least, vertical zoning of the Rb/Sr ratio which would be expected in the symmetrical model. The results reported here, which confirm the conclusions of Powell, et al (1965) show a decreasing Sr^{87}/Sr^{86} ratio with decreasing SiO_2 content for major rock types (tholeiites, alkali basalt series, and nepheline basalts).

The theoretical model of Kushiro and Kuno (1963) showed how magmas of varying silica content may originate under different pressure conditions due to the melting behavior of enstatite in periodotite or garnet in garnet peridotite. The data reported here support the theory that the tholeiites are

derived by partial melting from shallow depths, alkali basalts from slightly greater depths, and nepheline basalts from even deeper material.

The refractory residuum remaining in the upper mantle source regions following derivation of the oceanic basalt magmas may be mineralogically similar to the ultramafic inclusions often found in oceanic basalts. The trace elements in these inclusions may have equilibrated with the enclosing basalt (as is indicated by similar Sr^{87}/Sr^{86} ratios) and therefore would not give a true picture of the Rb-Sr relationships in the upper mantle residuum.

Potassium-rubidium relationships determined for the oceanic basalts in this study agree with those reported by Gast (1965). There is a general decrease in the K/Rb ratio with increasing K_2O content for major rock types, but there is no decrease in the Hawaiian alkali series. Both potassium and rubidium concentrations are low in the subalkaline basalts and yet their K/Rb ratios are very high (similar to the achondrites) which suggests that they are relatively undifferentiated or, if they are differentiated potassium and rubidium are not significantly fractionated.

The rubidium-strontium relationships obtained for the oceanic basalts are more favorable to an earth that has been more complex in its development than originally postulated. This complexity is compatible with the asymmetrical model for

development.

Continental Regions. Although no Rb-Sr measurements were made on continental basalts in this study, the results reported in the literature should be examined to see how they support the asymmetrical model.

One of the strongest arguments for the asymmetrical development of the earth but which is also the most serious objection to continental drift, is the observed equality of heat flow from the continental and oceanic regions. It is from these observations that geochemists have concluded that the continental upper mantle is more highly differentiated than the oceanic upper mantle. However, there are still many questions that have arisen concerning the precision of heat flow measurements and their interpretations.

The observed higher Sr^{87}/Sr^{86} ratios and rubidium and strontium abundances in continental subalkaline basalts as opposed to their oceanic counterparts are not expected to be indicative of the Rb-Sr relationships in their upper mantle source regions but are most probably due to crustal contamination. The high Sr^{87}/Sr^{86} ratios observed in continental igneous and metamorphic rocks are due to a combination of the early development of the continental plates, and addition by convection of rubidium (and strontium) removed from the oceanic upper mantle, and the redistribution of rubidium in the geologic cycle.

The fact that Recent volcanic activity is concentrated

in the oceanic regions or at their peripheries is another indication of the asymmetry of the earth's upper mantle.

Analysis of alpine-type ultramafics show that these rocks have very low concentrations of both rubidium and strontium and therefore may be the refractory residual material remaining in the upper mantle following the generation and removal of the continental basalt magmas. It is almost certainly true that these ultramafics were not the parental material of the basalt magmas nor were they a residuum from the generation of Recent oceanic basalt magmas.

Conclusions

The rubidium-strontium isotopic evidence is compatible with a complex differentiation history of the earth, therefore in interpreting the Rb-Sr data from oceanic basalts, asymmetrical differentiation should be kept in mind.

Conclusions arising from the rubidium-strontium relationships in oceanic basalts are:

1. Oceanic basalt source regions are generally quite uniform with respect to their Rb/Sr ratio but small scale regional Rb/Sr heterogeneities, produced early in the earth's differentiation history, are present.
2. Alkali and subalkaline basalt magmas are derived from similar source material in the upper mantle.

Slightly different depths of origin are indicated.

3. The Recent subalkaline basalts forming the ocean floors and ridges were generated by the partial or complete melting of material that had been depleted in rubidium relative to strontium at an earlier stage in the differentiation of the earth.
4. Recent oceanic alkalic and acidic basalts owe their enrichments of rubidium and strontium and their high Rb/Sr ratios (relative to subalkaline basalts) to geologic processes that occurred at the time of their generation or subsequent differentiation.

These rubidium-strontium data support a model in which the trace element abundances in the oceanic and continental upper mantle are very different. These differences reflect, at depth, the asymmetrical distributions of the continents and ocean basins. Asymmetries of crustal and upper mantle material are most easily explained by the asymmetrical model for the differentiation of the earth --one in which there has been continuing convection.

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APPENDIX A

I. Locations and Descriptions of Specimens

II. Chemical Analyses and Norms

I. Location and Descriptions of Specimens

Hawaiian Islands

R6328

Name: Melabasalt Porphyry; Koolau series

Location: 157°39'42"W 21°18'46"N, road cut Makapuu Point, Oahu

Description: Fine-grained vesicular, porphyritic; olivine and orthopyroxene phenocrysts in an intersertal groundmass containing plagioclase (An_{60}), pigeonitic pyroxene, 15% glass, and 5-20% ore minerals.

Chemical Analysis: Wentworth and Winchell (1947) Table 4 (#9948)

R6336

Name: Basalt Porphyry; Koolau series

Location: 157°58'18"W 21°28'29"N, Waiahole Valley, Oahu.

Description: Fine-grained, few vesicles and phenocrysts; intergranular porphyritic texture, 10% plagioclase phenocrysts, 10% hypersthene. Some olivine phenocrysts with iddingsite rims. Groundmass 30% plagioclase (An_{60}), pigeonite; minor glass and iron oxides.

Chemical Analysis: Wentworth and Winchell (1947) Table 4 (#10396)

R6337 Name: Diabase, Koolau (intrusive) series

Location: 157°47'15"W 21°18'15"N, Palolo quarry, Oahu.

Description: Medium-grained; intergranular texture, locally diabasic. Contains plagioclase, augite, hypersthene, minor olivine, ore minerals, and interstitial alkalic feldspar in part a microperthitic intergrowth. Small acicular apatite grains in feldspar. Hypersthene occasionally contains cores of olivine, and occasionally rimmed with augite. Plagioclase zoned from intermediate labradorite in center to andesine on outside.

Chemical Analysis: Wentworth and Winchell (1947), Table 4 (#10398)

6338 Name: Melabasalt, Koolau series

Location: 157°39'19"W 21°18'38"N, Makapuu Head, Oahu.

Description: Vesicular, nonporphyritic; few olivine phenocrysts partly resorbed and altered to iddingsite. Intersertal groundmass of plagioclase (medium labradorite), pryoxene, ore minerals, and glass. Pyroxene is pigeonite with minor microphenocrysts of hypersthene.

Chemical Analysis: Wentworth and Winchell (1947), Table 4 (#10403)

R6332

Name: Ankaramite; Kula series

Location: Haleakala crater, Maui

Description: Porphyritic with olivine and augite phenocrysts; 21% augite phenocrysts, 20.5% olivine phenocrysts. Intersertal groundmass, 25% plagioclase, 18% clinopyroxene, 5% olivine, 9% iron ore.

Chemical Analysis: MacDonald and Powers (1946), Table 1 (#1101)

R6333 Name: Hawaiite; Kula series.

Location: Haleakala crater, Maui

Description: Nonporphyritic, few small vesicles; intergranular texture. Volumetric percentages of minerals are: Plagioclase 74%, pyroxene 11.1%, olivine 3.9%, iron ore 8.0%, biotite 1.1%, apatite 1.8%. Average composition of the plagioclase is probably andesine. Pyroxene is augite.

Chemical Analysis: MacDonald and Powers (1946), Table 1 (#1102)

R6334 Name: Mugearite; Kula series

Location: Haleakala crater, Maui

Description: Hornblende bearing oligoclase andesite; slightly porphyritic. Basaltic hornblende and sodic labradorite phenocrysts. Groundmass of poikilitic feldspar containing clinopyroxene, olivine, iron ore, and apatite. Larger feldspar grains zone from medium andesine to medium oligoclase.

Chemical Analysis: MacDonald and Powers (1946), Table 1 (#1104)

R6335 Name: Andesite; Kula series

Location: Quarry Haleakala volcanoe, Maui

Description: Rare phenocrysts of olivine up to 1 mm. intergranular texture; approximate mineral composition, plagioclase (averaging sodic andesine) 53%, augite 24%, olivine 10%, iron ore 12%, apatite 1%, biotite < 1%.

Chemical Analysis: MacDonald and Powers (1946), Table 1 (#1106)

R6329 Name: Nepheline-melilite basalt; Honolulu series

Location: 157°50'10"W 21°22'12"N, Kalihi flow in Kalihi stream channel at Water Reserve boundary, Oahu.

Description: Dark gray, massive basalt with dunite nodules. Dunite segregations eliminated from the sample. Some olivine phenocrysts present.

Chemical Analysis: Winchell (1947), Table 7 (#9960)

R6330 Name: Linosaite; Honolulu series

Location: 157°41'38"W 21°16'33"N, southwest edge of flow in gulch north of Hanuauma Bay, Koko Head, Oahu.

Description: Dark gray, visicular, slightly porphyritic.

Chemical Analysis: Winchell (1947), Table 7 (#9962)

R6331 Name: Nepheline basanite; Honolulu series

Location: 157°47'45"W 21°15'30"N, south tip of Black Point (Kupikipikio), Oahu.

Description: Very dark vesicular basalt with inconspicuous olivine phenocrysts.

Chemical Analysis: Winchell (1947), Table 7 (#9982)

R6324 Name: Nepheline basalt; Honolulu series

Location: 157°50'50"W 21°19'43"N, lower Nuuana Stream above Kapena Pool.

Description: Dark gray, fine-grained; 2 mm olivine phenocrysts; rare vesicles.

Chemical Analysis: Winchell (1947), Table 7 (#9961)

R6322 Name: Basanitoid; Honolulu series

Location: Lava of Kaimuki shield, 18th and Kilauea Avenues, Honolulu, Oahu.

Description: No petrographic description.

Chemical Analysis: MacDonald and Katsura (1964), Table 8 (C-32)

R6321 Name: Hawaiite; Laupahoehoe series

Location: Roadcut on Kamuela-Kona Road 1.6 miles southwest of Popoo Gulch, Mauna Kea, Hawaii.

Description: No petrographic description.

Chemical Analysis: MacDonald and Katsura (1964), Table 4 (C-72)

R6323 Name: Tholeiite; Kau series

Location: Lava of 1881 eruption of Mauna Loa, at Kaumana, Hawaii.

Description: No petrographic description.

Chemical Analysis: MacDonald and Katsura (1964) Table 8 (#2201)

R6325 Name: Alkali olivine basalt; Hualalai series

Location: North of Keauhou, Hualalai, Hawaii.

Description: No petrographic description.

Chemical Analysis: Muir and Tilley (1961), Table 2, Column 1.

R6326 Name: Trachyte

Location: Puu Anahala village, Hulalai volcanoe, Honolulu, Oahu.

Description: No petrographic description.

Chemical Analysis: Washington (1923) Pg. 108, Analysis #2.

R6327 Name: Nephelite-melilite basalt

Location: Moliili Quarry, Honolulu, Oahu

Description: Fine-grained, holocrystalline 20% euhedral-olivine crystals. Augite less abundant, reddish or yellowish-brown pleochroic. Melilite in basal tablets, colorless.

Chemical Analysis: Cross (1915) Page 22, Analysis # 40.

Tristan da Cunha

R6102 Name: Leucite trachybasalt

Location: From plug 100 yards east of summit crater lake, Tristan da Cunha.

Description: No petrographic description.

Chemical Analysis: Baker, et al (1964) Table 7, British Museum Number B.M., 1962, 128 (351).

R6103 Name: Trachyandesite

Location: Lava of 1961 eruption, northeast extremity of lava field

Description: No petrographic description.

Chemical Analysis: Baker, et al (1964) Table 7, British Museum Number B.M., 1962, 128 (627).

Canary Islands (No names, chemical analyses or petrographic descriptions available)

R5810	Hierro Islands	Florida State Numbers:	H19-1
R5811	Hierro Islands		H20-2
R5814	Gomera Island		G10-2
R5816	Gomera Island		G18-2
R5817	Teneriffe Island		TF9-Z
R5819	Teneriffe Island		TF22-1
R5832	Madeira Island		M25-2

East Pacific Rise Subalkaline Dredge Basalts

R5950 Porphyritic bytownite basalt with glassy microcrystalline groundmass.

Location: 7°47'S 108°10'W depth 1700m.

Chemical Analysis: Engel and Engel (1964a) Table 1 Column D1 La Jolla Number PD1P

R5951 Glassy to microcrystalline basalt

Location: 12°52'S 110°57'W depth 2300m.

Chemical Analysis: Engel and Engel (1964a) Table 1 Column D3 La Jolla Number PD3

5952 Fine-grained basalt

Location: 18°25'S 110°57'W depth 3200m.

Chemical Analysis: Engel and Engel (1964a) Table 1 Column D4 La Jolla Number PD4G

Molokai Fracture Zone Dredge Basalts

R5964, R5965, R5966, R5967 Subalkaline basalts dredged from the Molokai fracture zone. No chemical analysis or petrographic descriptions available. La Jolla Numbers P1P, P2P, P3P, P4P respectively.

Mid-Atlantic Ridge Subalkaline Dredge Basalts

R5953 No description

Location: 5°47'S 11°25'W depth 2380m.

Chemical Analysis: Engel and Engel (1964b) Table 1, Column D3 La Jolla Number AD3-2

R5954 No description

Location: 9°39'N 40°27'W depth 2388m.

Chemical Analysis: Engel and Engel (1964b) Table 1, Column D5-5 La Jolla Number AD5-5

R5955 No description

Location: 9°39'N 40°27'W

Chemical Analysis: Engel and Engel (1964b) Table 1, Column D5-18 La Jolla Number AD5-18

R5973 Subalkaline greenstone

Location: About 22°N on mid-Atlantic Ridge.

Chemical Analysis: Melson and Bowen, personal communication.

Woods' Hole Number: Ch 44-2-7

R5974 Subalkaline basalt

Location: About 22°N on mid-Atlantic Ridge

Chemical Analysis: Melson and Bowen, personal communication.

Woods' Hole Number: Ch 44-2-2

R5975 Subalkaline greenstone

Location: About 22°N on mid-Atlantic Ridge.

Chemical Analysis: Melson and Bowen, personal communication.

Woods' Hole Number: Ch 44-2-1

R5976 Subalkaline metabasalt

Location: About 22°N on mid-Atlantic Ridge.

Description: Brecciated metabasalt with abundant albitized plagioclase phenocrysts.

Chemical Analysis: Melson and Bowen, personal communication.

Woods' Hole Number: Ch 44-3-7

R5977 Subalkaline greenstone

Location: About 22°N on mid-Atlantic Ridge.

Chemical Analysis: Melson and Bowen, personal communication.

Woods' Hole Number: Ch 44-3-10

R5978 High-alumina basalt

Location: 22°56'N 46°35'W

Description: Glassy upper-left margin of basalt boulder described by Cifelli (1965) and Nicholls, Nalwalk and Hays (1964).

Woods' Hole Number: Ch 17-Boulder Piece A.

R5979 High-alumina basalt

Location: Same as R5978

Description: Halfway into the center of basalt boulder above.

Woods' Hole Number: Ch 17-Boulder Piece B.

R5980 High-alumina basalt

Location: Same as R5978

Description: Porphyritic center of basalt boulder

Chemical Analysis: Nicholls, Nalwalk, and Hays (1964), Table 1, column 6. Norm, Table III, column 6.

Woods' Hole Number: Ch17-Boulder Piece C.

Hawaiian Islands

	R6328	R6336	R6337	R6338
SiO_2	49.62	48.74	52.30	51.94
TiO_2	1.51	2.42	1.68	2.58
Al_2O_3	12.68	15.98	14.80	14.18
Fe_2O_3	3.21	4.14	3.12	2.81
FeO	7.60	7.16	7.30	8.14
MnO	.09	.06	.05	.08
MgO	13.86	6.96	6.72	7.21
CaO	7.48	9.90	7.98	9.24
Na_2O	2.36	2.77	3.78	2.52
K_2O	.15	.22	.60	.35
H_2O^+	.67	1.19	.64	.59
H_2O^-	.34	.70	.23	.12
CO_2				
P_2O_5	.04	.08	.66	.35
SO_3	.05	.09		
BaO				
SrO				
Cr_2O_3	.19	.04		.04
	99.85	100.45	99.86	100.15

Norms

Qt		1.62	2.16	6.24
Or	1.11	1.11	3.34	2.22
Ab	19.91	23.58	31.96	20.96
An	23.63	30.58	21.68	26.41
Wo]	5.68	7.42	5.57	7.31
En] Di	4.10	5.10	3.50	4.60
Fs]	1.06	1.72	1.52	2.24
En]	22.90	12.30	13.30	13.40
Fs] Hy	5.94	4.22	6.47	6.34
Fo]	5.32			
Fa] Ol	1.43			
Mt	4.64	6.03	4.41	4.18
Il	2.89	4.56	3.19	4.86
Ap		.34	1.68	.67
Cm	.22			
	98.83	98.58	98.78	99.43

	R6332	R6333	R6334	R6335
SiO_2	42.30	47.64	54.14	47.78
TiO_2	2.41	3.44	1.81	4.11
Al_2O_3	10.52	17.62	17.82	16.32
Fe_2O_3	4.22	5.62	3.90	4.37
FeO	9.70	5.48	5.34	8.43
MnO	0.06	0.08	0.08	0.08
MgO	14.90	4.19	1.88	5.06
CaO	12.08	7.90	4.94	7.58
Na_2O	1.56	4.72	6.24	4.18
K_2O	0.42	1.60	2.72	1.30
H_2O^+	0.87	0.45	0.24	0.37
H_2O^-	0.45	0.09	0.03	0.06
CO_2				
P_2O_5	0.33	0.87	0.61	0.61
SO_3		0.03	0.04	0.02
BaO				
SrO				
Cr_2O_3	0.11			
	99.93	99.73	99.79	100.27
		Norms		
Or	2.22	9.45	16.12	7.78
Ab	7.34	34.06	46.11	35.11
An	20.57	25.85	12.51	21.68
Ne	3.12	3.12	3.69	0.28
Wo (Di)	15.66	3.25	3.48	5.22
En (Di)	11.10	2.80	1.90	3.50
Fs (Di)	3.17		1.45	1.32
Fo	18.27	5.39	1.96	6.37
Fa	5.61		1.63	2.86
Mt	6.03	7.66	5.57	6.50
Il	4.56	6.54	3.50	7.75
Ap	0.67	2.02	1.34	1.34
Hm		0.32		
	98.32	100.46	99.26	99.71

	R6330	R6324	R6329	R6331
SiO_2	45.13	38.57	36.75	42.86
TiO_2	2.94	2.79	2.41	2.94
Al_2O_3	16.40	11.71	11.98	11.46
Fe_2O_3	3.42	5.21	6.05	3.34
FeO	8.17	7.78	7.45	9.03
MnO	.07	.11	.08	.13
MgO	5.52	13.08	12.08	13.61
CaO	11.30	12.84	13.81	11.24
Na_2O	3.62	4.22	4.75	3.02
K_2O	1.02	1.20	.91	.93
H_2O^+	1.16	.59	1.61	.44
H_2O^-	.42	.19	.36	.12
CO_2	.05	.27		
P_2O_5	.66	1.11	1.41	.52
SO_3	.17	.17	.17	.22
BaO	.06	.03	.13	.04
SrO				
Cr_2O_3		.06	.03	.04
	100.11	99.98	99.98	99.94

Norms

Or	6.12			5.56
Ab	19.91			5.76
An	25.58	9.45	8.90	15.29
Lc		5.67	4.36	
Ne	5.68	19.31	21.58	10.51
Wo] Di	10.67	14.15	11.14	15.43
En] Di	6.50	10.80	8.60	11.10
Fs] Di	3.56	1.85	1.32	2.90
Fo] Ol	5.04	15.12	13.86	16.10
Fa] Ol	3.06	2.86	4.49	4.69
Cs		3.44	7.40	
Mt	4.87	7.66	8.82	4.87
Il	5.62	5.32	4.56	5.62
Ap	1.68	2.69	3.36	1.34
	98.29	98.32	98.39	99.17

	R6321	R6322	R6323	R6325
SiO_2	47.99	43.12	51.85	46.53
TiO_2	2.62	2.11	1.93	2.28
Al_2O_3	19.36	13.36	14.04	14.31
Fe_2O_3	5.83	2.45	1.56	3.16
FeO	5.17	10.53	9.16	9.81
MnO	0.21	0.19	0.17	0.18
MgO	4.39	13.07	7.85	9.54
CaO	6.54	11.02	10.45	10.32
Na_2O	4.58	2.55	2.07	2.85
K_2O	1.82	0.60	0.37	0.84
H_2O^+	0.33	0.38	0.24	
H_2O^-	0.17	0.40	0.27	
CO_2				
P_2O_5	0.63	0.38	0.22	0.28
SO_3				
BaO				
SrO				
Cr_2O_3				
	99.64	100.16	100.18	100.10

Norms

Q				3.42
Or		10.56	3.34	2.22
Ab		36.15	10.48	18.34
An		26.97	23.35	27.24
Ne		1.42	5.96	
Wo	Di	0.81	11.83	9.78
En	Di	0.61	7.70	5.80
Fs	Di	0.13	3.30	3.70
En	Hy			13.80
Fs	Hy			8.84
Fe	Ol	7.28	17.50	
Fa	Ol	0.51	8.46	
Mt		8.35	3.48	2.32
Il		5.02	3.95	3.65
Ap		1.34	1.01	0.34
		99.15	100.36	99.45

	R6326	R6327
SiO_2	62.02	36.34
TiO_2	0.31	2.87
Al_2O_3	18.71	10.14
Fe_2O_3	4.30	6.53
FeO	0.10	10.66
MnO	0.15	0.20
MgO	0.40	10.68
CaO	0.86	13.10
Na_2O	6.90	4.54
K_2O	4.93	1.78
H_2O^+	0.80	1.00
H_2O^-	0.31	1.00
CO_2		0.15
P_2O_5	0.24	1.02
SO_3	0.02	0.04
BaO	0.02	
SrO		
Cr_2O_3		
ZrO_2	0.06	
	100.13	100.05
	Norms	
Q	1.80	
Or	28.91	
Ab	58.16	
An	2.22	1.67
Ne		21.02
C	1.22	.31
Le		8.28
Di		17.39
Hy	1.00	
Ol		20.23
Ak		11.95
Mt		9.51
Il	0.15	5.47
Hm	4.30	
Ru	0.24	
Ap	0.67	2.35
H_2O		2.00
	98.67	100.18

East Pacific Rise

	R5950[1]	R5951[1]	R5952[1]
SiO_2	48.53	49.80	49.64
TiO_2	0.76	2.02	1.37
Al_2O_3	22.30	14.88	16.96
Fe_2O_3	0.69	1.55	1.35
FeO	4.82	10.24	7.85
MnO	0.16	0.21	0.18
MgO	7.14	6.74	8.37
CaO	12.86	10.72	12.01
Na_2O	2.18	2.91	2.75
K_2O	0.06	0.24	0.11
H_2O^+	0.38	0.54	0.30
H_2O^-	.01	.06	.01
CO_2			
P_2O_5	.07	.28	.09
	99.96	100.19	100.22

Norms

Or	.56	1.67	.56
Ab	18.34	24.63	23.06
An	50.87	26.69	31.69
Hy	12.46	14.96	7.11
Di	10.07	20.13	22.31
Ol	5.58	4.80	10.49
Il	1.52	3.80	2.58
Mt	.93	2.32	1.86
Ap	.16	.62	.19
	100.49	99.62	99.85

[1]Data from Engel and Engel (1964a)

Mid-Atlantic Ridge

	R5953	R5954	R5955
SiO_2	49.48	49.02	50.13
TiO_2	1.39	1.46	0.86
Al_2O_3	16.72	18.04	19.65
Fe_2O_3	1.16	1.58	1.86
FeO	7.58	6.22	4.77
MnO	0.19	0.13	0.12
MgO	8.20	7.85	5.95
CaO	11.14	11.51	12.57
Na_2O	2.66	2.92	2.77
K_2O	0.24	0.08	0.21
H_2O^+	.62	.64	.50
H_2O^-	.61	.57	.44
CO_2			
P_2O_5	.12	.12	.19
	100.11	100.14	100.02

Norms

Or	1.67	.56	1.11
Ab	22.53	24.63	23.56
An	32.80	35.86	40.59
Hy	11.26	6.88	11.27
Di	17.59	16.52	16.74
Ol	8.55	9.70	1.08
Il	2.58	2.74	1.67
Mt	1.62	2.32	2.78
Ap	.31	.31	.31
	98.91	99.52	99.11

	R5973[1]	R5974[2]	R5975[1]	R5976[1]	R5977[1]
SiO_2	47.00	49.10	49.74	51.70	48.39
Al_2O_3	15.61	15.27	16.52	14.70	19.85
Fe_2O_3	6.11	2.54	2.06	3.22	1.77
FeO	4.10	8.36	7.19	4.77	5.05
MnO	.19	0.20	.16	0.11	.08
MgO	10.67	8.09	7.41	7.13	7.11
CaO	5.34	10.61	11.69	10.76	12.32
Na_2O	3.27	2.86	2.70	3.95	2.37
K_2O	.14	0.25	.21	0.08	.05
H_2O^+	5.71	0.56	.52	1.93	1.50
H_2O^-	.32	0.25	.41	0.55	.31
TiO_2	1.39	1.73	1.53	0.99	.89
P_2O_5	.18	0.16	.06	0.08	.08
	100.03	99.98	100.20	99.97	99.78

Norms

Q	0.18				
Or	.56	1.67	1.11	.56	.28
Ab	27.77	24.10	23.06	33.54	19.91
An	25.58	28.08	32.23	21.96	43.51
Di		19.13	20.67	24.80	13.70
Hy	27.36	11.56	12.06	8.22	12.24
Ol		7.27	4.09	1.81	3.92
Il	2.58	3.34	2.89	1.82	1.67
Mt	8.82	3.71	3.02	4.64	2.55
Ap	0.31	.31	.12	.19	.19
Cor	0.71				
	93.87	99.17	99.25	97.54	97.97
H_2O(total)	6.03				
	99.90				

[1] Greenstone

[2] Basalt

Chemical Analyses of a Porphyritic Altered Basaltic Boulder from 22°56'N 46°35'W[1]

	Average of Boulder	Calculated Groundmass[2]
SiO_2	46.39	46.24
Al_2O_3	20.19	18.70
Fe_2O_3	7.31	8.12
FeO	2.87	3.19
MnO	0.12	0.13
MgO	4.59	5.10
CaO	11.48	10.92
Na_2O	2.82	2.89
K_2O	0.13	0.14
H_2O^+	1.15	1.28
H_2O^-	1.41	1.57
TiO_2	1.46	1.62
P_2O_5	0.06	0.07
Cl	.26[3]	
	100.18	99.96

Norms

Qt	2.35
Or	0.78
Ab	21.96
An	42.98
Di	10.86
Hy	6.45
Ol	
Mt	5.07
Il	2.77
Hm	3.82
Ap	0.14
others	2.98*
	100.16

[1] From Nicholls, Nalwalk, and Hays (1964) Table 1, Columns 6 and 7.

[2] Calculated from Column 1 by subtracting 10% phenocrysts of bytownite (An_{82}).

[3] Before making allowance for oxygen equivalence

* Includes NaCl and H_2O

Tristan da Cunha

	R6102	R6103
SiO_2	47.06	54.66
Al_2O_3	17.14	19.91
Fe_2O_3	3.29	3.07
FeO	6.65	2.73
MnO	0.18	0.18
MgO	4.35	1.10
CaO	9.00	5.56
Na_2O	4.08	5.85
K_2O	3.40	5.03
H_2O^+	0.37	0.00
H_2O^-	0.27	0.00
TiO_2	3.44	1.60
P_2O_5	0.75	0.29
Cl		6.23
F		0.10
	99.98	100.22

Norms

Or	20.10	29.72
Ab	15.45	31.14
An	18.42	14.10
Ne	10.33	9.03
Di	17.15	6.22
Ol	4.85	
Hy		
Wo		1.29
Mt	4.77	4.45
Il	6.53	3.03
Ap	1.77	0.67
H_2O^+	0.34	0.00
H_2O^-	0.27	0.00
	99.98	100.18*

*Includes 0.53 fluorite and halite

Minor Element Analyses* of Trachyandesite and Leucite Trachybasalt from Tristan da Cunha

	R6102	R6103
Nb	80ppm	140ppm
Mo	4	6
Zr	300	350
Ga	27	26
Cr		
U	280	110
Y	25	45
La	160	200
Be		
Ni		
Co	15	
Mn	1300	1600
Sr	1100	1400
Pb	10	14
Ba	1000	1300
Li	6	13
Rb	110	260

*Spectrographic Analyses from Baker, et al, 1964, Table 7.

APPENDIX B

A Reanalysis of Rubidium and Strontium in the Dun Mountain, New Zealand, Dunite

A portion of the Dun Mountain dunite sample R5433, analyzed previously by Roe (1964), was reanalyzed to see if the factor of ten discrepancy between values for strontium reported by Roe (1964) and Steuber and Murthy (1966) is real. This difference was consistent for all alpine-type ultramafics analyzed by both groups although the Dun Mountain dunite was the only locality studied in common. A direct comparison cannot be made between the results reported here and those reported by Roe because the samples are not identical. There should, however, be a close correspondence in the results.

Extreme caution was excercised in the preparation of this sample to keep the contamination levels of rubidium and strontium at a minimum. All chemical procedures were carried out under a dust hood (Shields, 1964) and rubidium and strontium blanks were prepared along with the sample as contamination controls.

Because the concentrations of both rubidium and strontium are low in dunite, a seven gram sample was processed to ensure an adequate supply of strontium.

Spike solutions were added to the sample as the first step in the chemical procedure. The sample was dissolved in 50 mls of vycor-distilled 6N HCl, centrifuged and decanted, and the liquid fraction stored in a covered polypropylene beaker. This procedure was repeated for the precipitate and the residue remaining after the second treatment was processed in HF, $HClO_4$, and 2NHCl acids in the same manner as the basalt samples described in Bence (1966).

The liquid fractions were combined, evaporated to 30 mls, diluted to 100 mls with demineralized water, divided into two fractions, and passed through separate ion exchange columns twice. Blanks were also treated in this manner.

The rubidium and strontium concentrations obtained in this analysis (Table 1) are in reasonable agreement with the results reported by Roe (1964). As a result of this independent study we believe that Roe's analyses were more correct than Steuber and Murthy's. However, it is difficult to draw further conclusions without making a reanalysis of the sample analyzed by Steuber and Murthy. It is possible that the discrepancies in the strontium abundances for the Dun Mountain dunite may be due to inhomogeneities between samples.

The variations between the Rb/Sr ratios reported here and those reported by Roe are due to the sensitivity of this ratio at very small concentrations of rubidium and strontium.

Table 1

Strontium and Rubidium Concentrations for Dun Mountain Dunite

	Sr ppm	Rb ppm	Rb/Sr
M.I.T. Group			
Roe (1964)	.320[1] .307[1]	.110[2] .071[2]	.996 .669
This investigation	.19[3]	.29[4]	1.53
La Jolla Group (Steuber and Murthy, 1966)	4.39[5]	.111[6]	0.025

Blank Corrections

1 .020 ppm

2 .015 ppm

3 .024 ppm

4 .008 ppm

5 0.05 ppm

6 0.002 ppm

References

Bence, A. E., The differentiation history of the earth by rubidium-strontium isotopic relationships, unpublished Ph.D. thesis, Mass. Inst. Tech., Dept. Geol. Geophys., 1966.

Roe, G. D., Rubidium-strontium analyses of ultramafic rocks and the origin of periodotites, M.I.T. 1381-12, Twelfth Annual Progress Report for 1964, 159-190, Dept. Geol. Geophys., 1964.

Steuber, A. M., and V. R. Murthy, Strontium isotope and alkali element abundances in ultramafic rocks, Geochim. et Cosmochim. Acta, in press, 1966.

APPENDIX C

Rare Earth and Rubidium-Strontium Relationships in Hawaiian Basalts

J-G. Schilling, A. E. Bence

Introduction

Rubidium/strontium ratios and strontium isotopic compositions have proven to be important research tools in studying the chemical evolution of the earth. They put constraints upon the composition of the source material and upon the time of differentiation processes. Nevertheless, due to the lack of complete understanding of trace element distribution and the factors influencing them, the applications of this method are limited. On the other hand, recent progress in rare earth geochemistry indicates that rare earth fractionation patterns may be sensitive indicators of the physico-chemical processes of differentiation. Thus a combination of the rare earth and rubidium-strontium methods would have the attributes of both methods and a more complete picture of the evolutionary history of the earth may be attained.

Rare earths, Rb, and Sr concentrations and Sr^{87}/Sr^{86} ratios are determined for the same sample powders of a suite of Hawaiian basalts. The results and interpretations are reported separately (Schilling and Winchester, 1966c;

Bence, 1966). Moreover, these samples have been analysed for major oxides and petrographic characteristics and geological occurrences have been discussed in great detail (Washington, 1923; MacDonald and Powers, 1946; Winchell, 1947; Wentworth and Winchell, 1947; Muir and Tilley, 1961; MacDonald and Katsura, 1964). Additional information on U, Th, and Pb abundances and Pb isotopic composition are available for several of the samples (Tatsumoto, 1966). The samples numbered "J.P." were previously analyzed for Sr^{87}/Sr^{86} ratios by Powell, Faure, and Hurley (1965).

Discussion

The Rb, Sr, La, and Yb concentrations and Sr^{87}/Sr^{86} ratios for each sample analyzed are given in Table 1. The concentrations of the other rare earths are available elsewhere (Schilling and Winchester, 1966c). On the basis of the Rb, Sr, and La concentrations, the basalts are divided into four groups. Figures 1, 2, and 3 are the variation diagrams of La versus Rb, La versus Sr, and Rb versus Sr respectively. The four groupings are particularly evident on the La-Rb variation diagram. The groupings are: the tholeiites which include a diabase from the Palolo quarry; the alkali series comprising an ankaramite, alkali-olivine basalts, basanite-basanitoids, hawaiites, and a mugearite; the nepheline-melilite basalts; and finally, a trachyte which stands by itself because of its high rubidium content. Although less evident, the other

FIGURE 1

Variation Diagram of La vs. Rb

in Hawaiian Volcanic Rocks

Δ	Nepheline-melilite basalt
✳	Mugearite
▫	Hawaiite
o	Basanite-basanitoid
◍	Alkali-olivine basalt and ankaramite
+	Tholeiite
▲	Trachyte

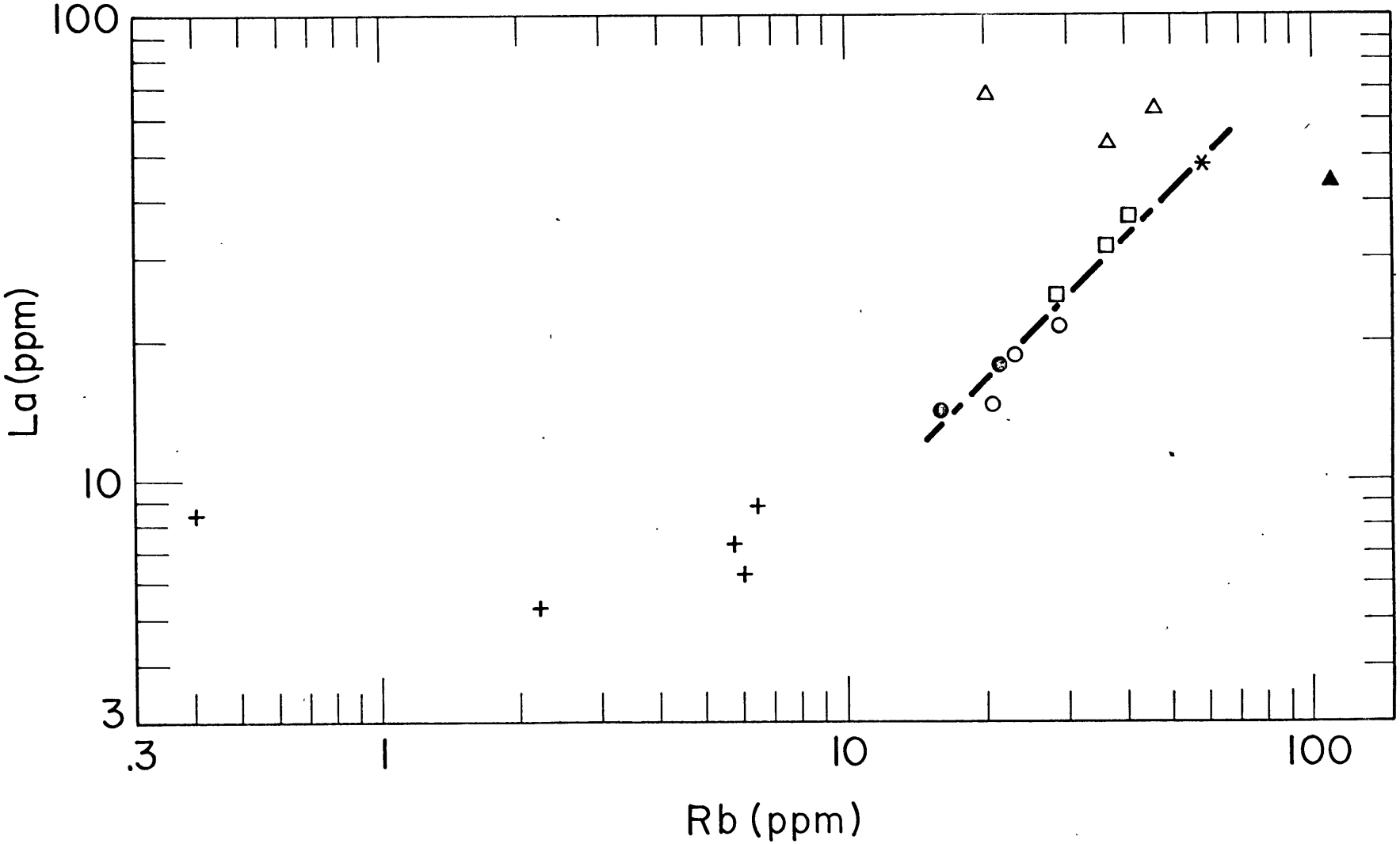

100
10
3
La (ppm)
.3
1
10
100
Rb (ppm)

FIGURE 2

Variation Diagram of La vs. Sr

in Hawaiian Volcanic Rocks

△ Nepheline-melilite basalt

✳ Mugearite

□ Hawaiite

○ Basanite-basanitoid

● Alkali-olivine basalt and ankaramite

+ Tholeiite

▲ Trachyte

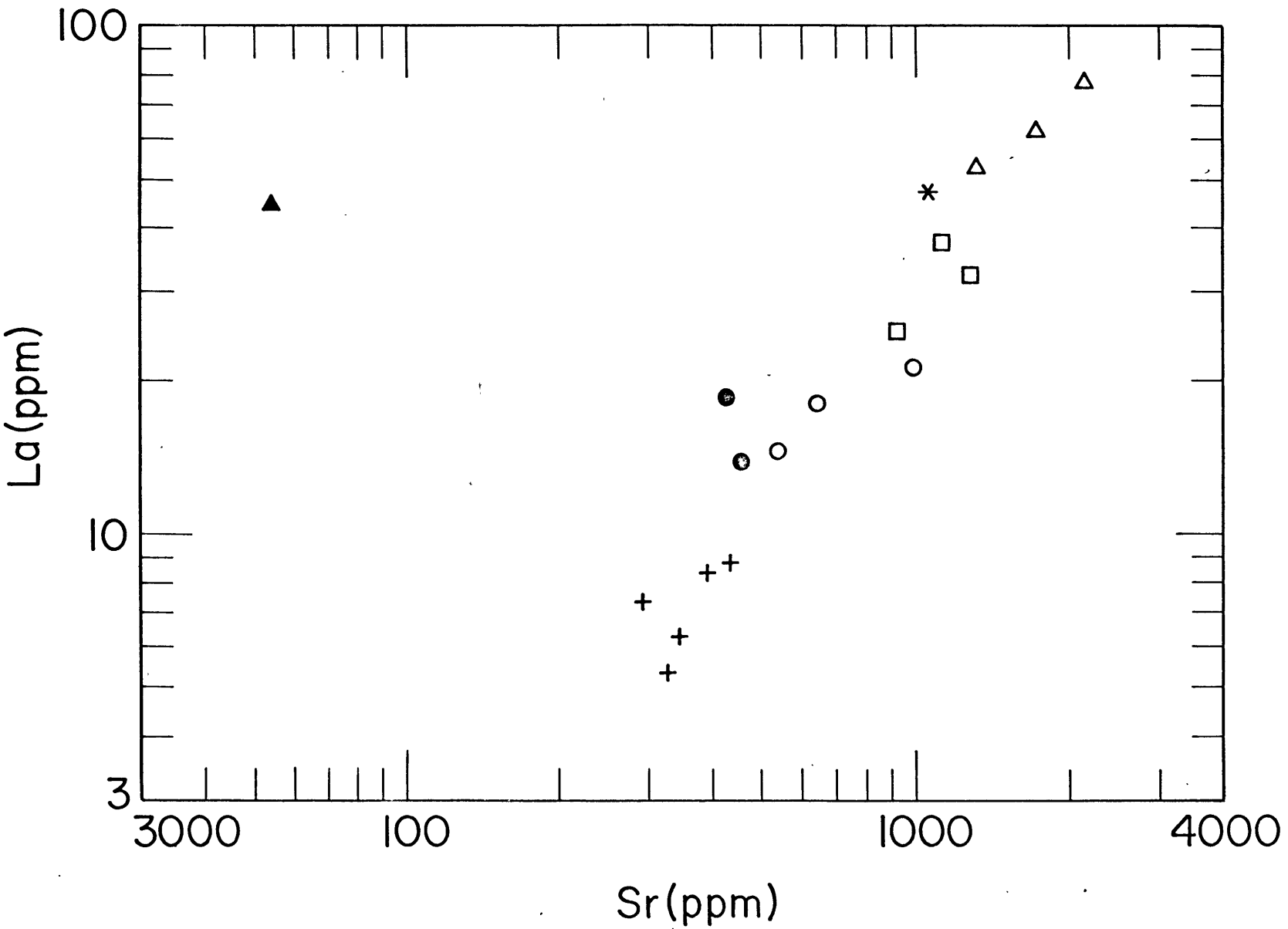
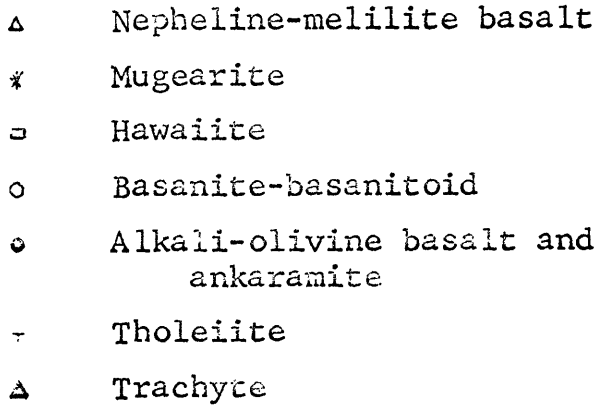
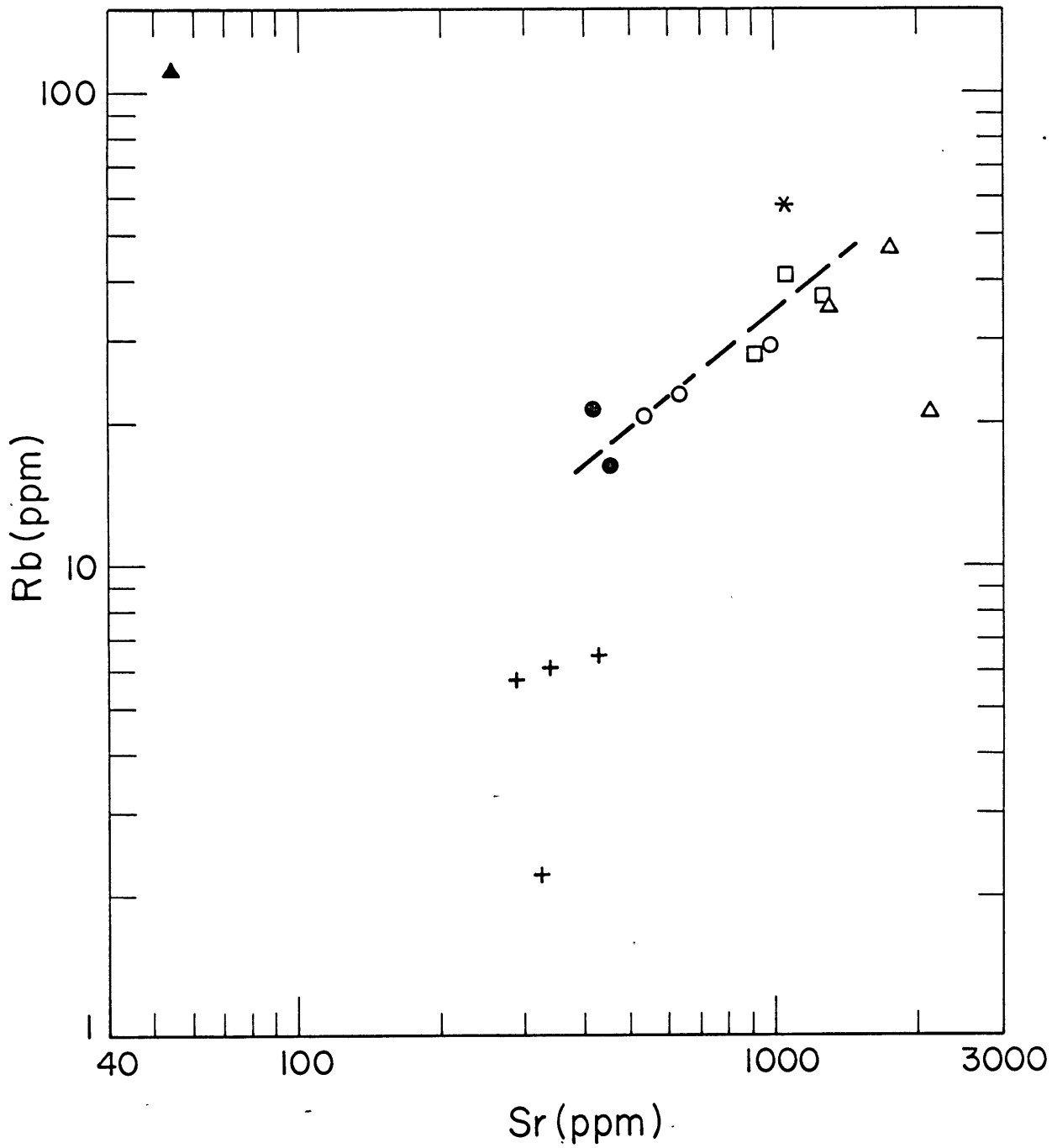

100
10
3
La(ppm)
3000
100
1000
4000
Sr(ppm)

FIGURE 3

Variation Diagram of Rb vs. Sr

in Hawaiian Volcanic Rocks




100
10
1
Rb (ppm)
40
100
1000
3000
Sr (ppm)

two diagrams show the same groupings. Schilling and Winchester (1966c) observed these same groupings independently from the relative rare earth patterns and from other variation diagrams of La against major oxides. It is remarkable that these groups based on trace element data alone correspond closely to well recognized petrological classifications. Moreover, these groupings also correspond closely with groupings based upon the Sr^{87}/Sr^{86} ratios with the exception of the trachyte, which cannot be distinguished from the alkali series on this basis alone (Bence, 1966), and the somewhat anomalous nepheline-melilite basalt #9960.

No systematic variation of La with Rb within the tholeiite suite or the nepheline-melilite basalt group is observed. In the alkali series, there is a sympathetic increase of La with Rb from the ankaramite to the mugearite. This coherence of two quite dissimilar elements may reflect simple mechanisms of differentiation for this series. The La-Rb variations suggest identical behavior for these two elements in the series. Many lines of evidence point to this series being the product of fractional crystallization, involving mainly olivine, augite, and plagioclase, in a magma originally of alkali-olivine composition.

Although the two ions are quite different in size (La^{+++} = 1.14Å and Rb^{+} = 1.47Å) both are larger than the largest major cation sites in the minerals involved. Thus, in

addition to filling of vacancies, if diadochic replacement of major cations by these cations has taken place, one would expect an increasing difficulty in replacing major cations by ions with increasing ionic radius. Rubidium should therefore increase more rapidly in the residual melt than lanthanum. This is not the case and it indicates that other parameters must influence the relative partitioning of these elements, (adsorption, charge differences or bonding, etc). The relatively larger scatter in the alkali series for La-Sr (Fig. 2), produced mainly by strontium variations, may be due to the fact that strontium has a close affinity for calcium sites and small variations in the proportions of Ca-bearing phenocrysts (augite, plagioclase) will influence noticeably the strontium abundances of the rocks.

A better coherence of Sr-La than Rb-La is observed for the tholeiitic and nepheline-melilite groups but there is a much greater dispersion of data for the alkali series.

Using the published K_2O analyses, we have observed that the K/Rb ratios seem to increase slightly with increasing K_2O content for the alkali series. Lessing, et al, 1963; Gast, 1965; and Taubeneck, 1965, show clearly that the K/Rb ratios for this series remain constant or slightly decrease with increasing K_2O. A redetermination of K_2O in these rocks seems advisable.

The data by Lessing, et al, 1963, show a marked decrease

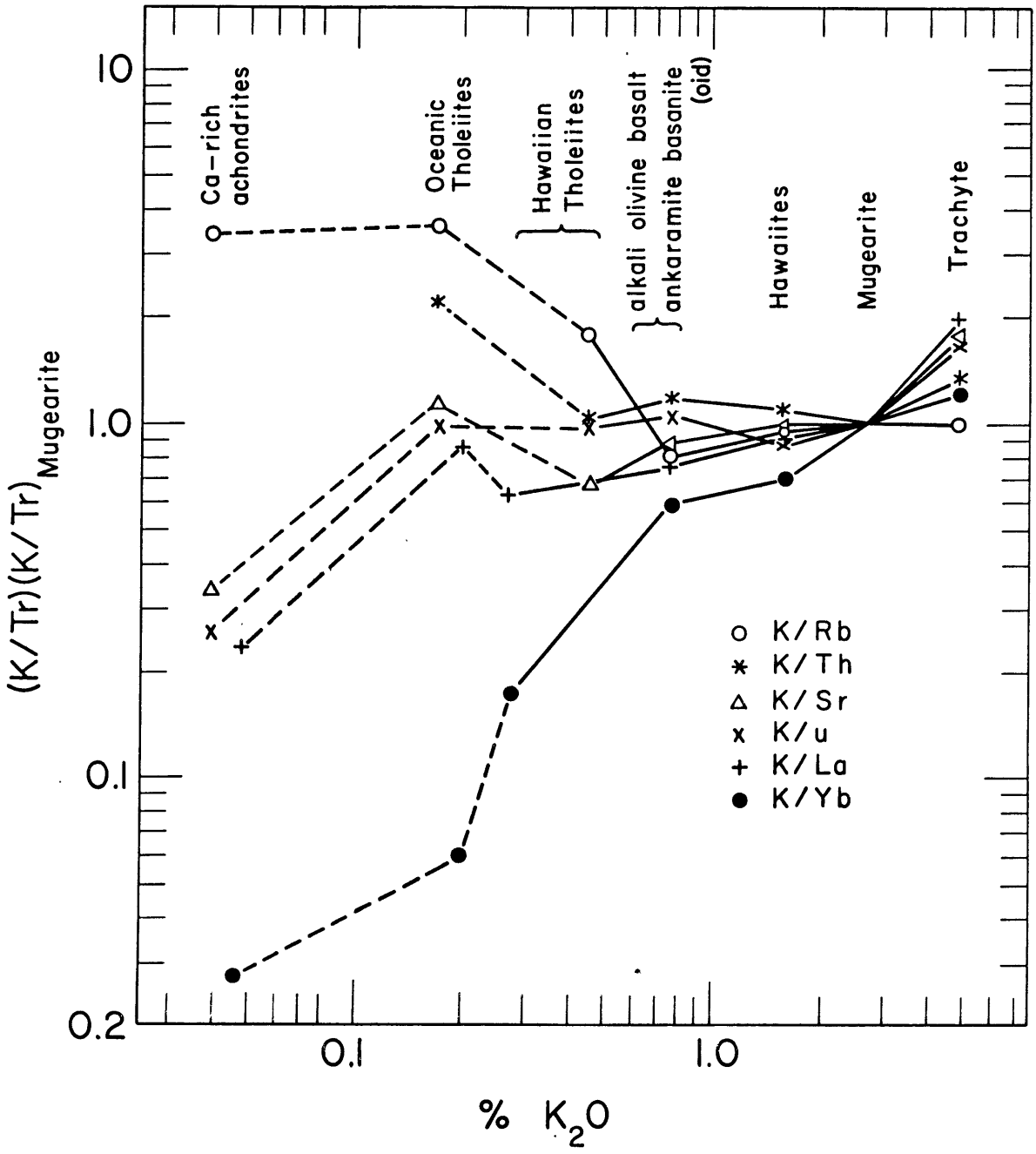
of K/Rb ratios with increasing K for lavas with K content higher than 2%. This corresponds to lavas grading from mugearite to trachyte. They attributed this decrease to some other process than crystal settling. Although this is quite possible for the trachyte, it should be remembered that anorthoclase is reported for lavas in the range hawaiite to mugearite (Muir and Tilley, 1961). This indicates clearly that the potassium content has reached its saturation point and, if equilibrium is maintained, the potassium concentration in the residual melt should stay constant or slightly decrease but certainly not increase. On the other hand, rubidium continues to be increasingly concentrated in the residual melt. Thus the K/Rb ratio is expected to decrease.

Special conditions for the origin of trachyte have been postulated (Turner and Verhoogen, 1962; Chayes, 1963; and Bailey and Schairer, 1966) where the importance of volatiles for the formation of these lavas is stressed. A marked increase of the heavy rare earths, which complex easily in solutions, has been noted by Schilling and Winchester (1966c) and in this respect confirms the importance of volatiles. If gaseous transfer is an important process for the formation of trachytic melt, one would expect a preferential enrichment of the more volatile trace alkali metals relative to the trace alkaline earths, the rare earths, Th, and U. Figure 4 illustrates the K/Rb, K/Sr, K/La, K/Yb, K/Th, and K/U ratios as functions of the K_2O

FIGURE 4

Relationships of K/Rb, K/Sr, K/U, K/La, K/Yb,

and K/Th Ratios in Oceanic Basalts


10
1.0
0.1
0.2
0.1
1.0
% K_2O
$(K/Tr)(K/Tr)_{Mugearite}$
Ca-rich achondrites
Oceanic Tholeiites
Hawaiian Tholeiites
alkali olivine basalt
ankaramite basanite
(oid)
Hawaiites
Mugearite
Trachyte
K/Rb
K/Th
K/Sr
K/u
K/La
K/Yb

content for the samples listed in Table 1. These ratios are normalized to the same ratios obtained for the mugearite in order to compare the relative behavior of the elements. The ratios are average values for the achondrites, oceanic tholeiites, Hawaiian tholeiites, Hawaiian alkaline series (excluding the hawaiite and mugearite), Hawaiian hawaiite, trachyte and mugearite. A horizontal line on this diagram indicates similar behavior for the element pairs. Thus from Figure 4 and Table 2, the K/Rb ratio from the mugearite to the trachyte remains constant indicating similar behaviors for K and Rb. On the other hand, K/Sr, K/U, K/La, K/Yb, and K/Th all increase markedly from the mugearite to the trachyte indicating a preferential increase of potassium and, by inference, other alkali metals relative to Sr, U, Th, and the rare earths. Table 2 also shows how Rb is preferentially enriched in the trachyte relative to the alkaline earths, rare earths, U and Th. In the alkali series one finds that Rb is slightly preferred to potassium in the trachyte which is in the same direction as emphasized by Gast (1965) for the loss of alkalis from the primitive earth. Thus, these data support the possibility that the trachyte may have formed by gaseous transfer.

The increasing activities in oceanographic research have resulted in the recovery of many interesting samples from the ocean depths especially from the oceanic ridges and

rises (Engel and Engel, 1964a,b; Nicholls, 1964; Nicholls, Nalwalk and Hays, 1964; Muir and Tilley, 1964; Engel, Engel, and Havens, 1965; and others). Chemical studies of these basalts have revealed important differences between these so-called "oceanic tholeiites" and the shield-building tholeiites from large volcanoes such as the Hawaiian Islands. These results have been interpreted in different ways by geochemists. Engel, Engel, and Havens (1965) suggest that the oceanic ridge basalts are the principal or only primary magma generated in the upper mantle under the oceans. They have argued that the shield-building tholeiites are derivatives of these primary melts followed by a thin capping of alkaline basalts. Frey and Haskins (1964) on the basis of relative rare earth patterns suggest that these basalts are "nearly undisturbed rare earth distribution patterns" and these "oceanic basalts are decidedly primitive". Further scrutiny of the rare earth abundance patterns of the oceanic and Hawaiian lavas have lead Schilling and Winchester (1966b and c) to object to such suggestions.

Figure 4 shows the change of K/Rb, K/Sr, K/Th, K/U, K/La, and K/Yb ratios between oceanic tholeiites and the Hawaiian tholeiites. Except for K/Rb and K/Yb ratios, which behave as expected from geochemical reasoning, the change of K/Th, K/U, K/La and K/Sr ratios is anomalous. The ratios change in the opposite direction from what is expected for fractional

crystallization, from the observation of the alkali series. Although from the absolute abundances of Rb, Sr, La, U, Th in the two types of tholeiites, it cannot be denied that the Hawaiian tholeiite (Engel, et al's intermediate type) could be derived from the oceanic tholeiitic magma, the change of these ratios indicates that fractional crystallization apparently cannot be the operative process. The high abundances of the heavy rare earths (those with the smallest ionic radii), which are as high as their abundances in thrachyte-mugearite differentiates and many granites, also strontly indicate that processes other than fractional crystallization must be considered if shield-building tholeiites need to be derived from the oceanic tholeiites.

The strontium isotope data for the Hawaiian tholeiites and the ridge basalts (Bence, 1966) show that there are small but marked differences in the Sr^{87}/Sr^{86} ratios for the two types of tholeiite. The Hawaiian tholeiites tend to have higher Sr^{87}/Sr^{86} ratios than their ridge counterparts. This may be an indication that the two are derived from different depths in an upper mantle that has a decreasing Rb/Sr with depth or it may be a reflection of latteral variations of Rb/Sr ratios in the upper mantle. Whatever the explanation, it is obvious that one cannot be a derivative of the other and they must originate from different source regions, which are characterized by different Rb/Sr ratios. The Rb/Sr ratios for the two tholeiite magmas are identical within the limits of precision;

but the absolute abundances of both elements are lower in the oceanic tholeiites

Therefore, on the basis of the heavy rare earth data, and the other ratios discussed above and possibly Sr^{87}/Sr^{86} ratios, it seems more reasonable to assume independent origins for the oceanic ridge and shield-building tholeiites. Thus, it appears that different fractionation processes must have been operative for the formation of these two lava types; or alternatively, they are derived from different source regions. One of us (JGS) has emphasized the possible effects of volatiles and environmental pressures during the extrusion of the oceanic lavas, and the possible presence of hornblende within the source region of the upper mantle (Schilling and Winchester, 1966b, and Nicholls, 1965). Zone melting as an alternative process was also considered.

Finally, generalizations on relative partition coefficients and ionic size (Masuda, 1965), although interesting, should be made with care. The reversal of the relative behaviors of some trace elements indicate that physico-chemical processes of differentiation, other than fractional crystallization, may affect the relative fractionation of these trace elements in very different ways than are predicted on the basis of ionic size and charge alone (Schilling and Winchester, 1966b).

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Table 1

K, Rb, Sr, La and Yb Abundances and Sr^{87}/Sr^{86} Ratios in Hawaiian Basalts

Group	Sample Number	Name	K ppm	Sr ppm	Rb ppm	La ppm	Yb ppm	Sr^{87}/Sr^{86}
Tholeiite	9948	olivine tholeiite	1245	329	2.18	5.30	1.26	.7048
	J.P.12	tholeiite	3070	290	5.73	7.22	1.85	.7038
	10396	tholeiite	1826	396	0.48	8.41	1.81	.7048
	10403	tholeiite	2905	432	6.43	8.78	2.06	.7046
	10398	diabase	4980	346	5.99	6.24	1.45	.7043
Alkali	1101	ankaramite	3480	453	16.3	13.91	1.40	.7040
	J.P.14	alkali olivine basalt	6970	419	21.4	17.76	1.63	.7030
	J.P.11	basanitoid	4980	539	20.6	14.49	1.14	.7028
	9962	linosaite	8460	992	28.9	21.29	1.82	.7037
	9982	nepheline basanite	7720	635	22.9	18.08	1.23	.7035
	J.P.10	hawaiite	15100	1260	36.6	31.65	2.74	.7035
	1102	hawaiite	13280	1107	40.2	36.09	2.44	.7044
	1106	andesite	10790	908	28.3	24.59	2.40	.7031
	1104	mugearite	22580	1061	58.4	47.98	3.08	.7046
Trachyte	J.P.15	trachyte	40900	5415	113.8	44.13	4.56	.7033
Nepheline	J.P.16	melilite nepheline basalt	14780	1752	46.6	62.61	.899	.7027
	J.P.13	nepheline basalt	9960	1303	36.2	51.96	2.01	.7030
	9960	nepheline melilite basalt	7550	2150	20.9	78.07	1.96	.7043

Table 2

	Mugearite	Trachyte	Trachyte / Mugearite		Mugearite	Trachyte	Trachyte / Mugearite
K/Rb	387	259	.93				
K/Sr	21.3	751	35.2	Rb/Sr	.055	2.09	38.0
K/Th	3670	5350	1.46	Rb/Th	9.85	14.9	1.51
K/U	9900	26950	2.72	Rb/U	26.5	75	2.83
K/La	471	927	1.97	Rb/La	1.22	2.58	2.11
K/Yb	7330	8973	1.22	Rb/Yb	19.0	25.0	1.31

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